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Low-melting organosilicon monomers of high molecular weight

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LOW-MELTING ORGANOSILICON MONOMERS OF HIGH MOLECULAR WEIGHT

by

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INTRODUCTION

The chemistry of organosilicon compounds has been studied for almost one hundred years[1]. Until the discovery of industrial applications for the polymeric silicones, most of the research efforts were directed toward the preparation of organosilicon monomers. When it was found that the silicones had high thermal stability, small change in viscosity with change in temperature and other desirable properties, the volume of research increased (especially in industrial laboratories) and was directed mainly toward the preparation of polymeric materials or of monomers suitable for polymerization. Because of the poor lubricating properties of the silicones, and because of the need for high-temperature thermally-stable and radiation-resistant lubricants and hydraulic fluids, studies were initiated in This Laboratory (under the auspices of the U.S. Air Force) on the preparation and properties of high-molecular weight organosilicon monomers. It was felt that such materials might be superior in some respects to the silicones or to other compounds for the previously described applications. Some of the early work on this project has shown that thermally-stable organosilicon monomers can be prepared. However, most of the compounds which have been synthesized have been found to be relatively high-melting solids and therefore unsuitable for use as lubricants or hydraulic fluids.

The study presented in this dissertation was undertaken in an effort

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[1]For some of the earliest work on organosilicon compounds, see C. Friedel and J. M. Crafts, Ann., 127, 28 (1863) and A. Ladenburg, Ann., 162, 300 (1872).

to produce high-molecular weight organosilicon monomers with low melting points which retained the thermal-stability of the previously synthesized compounds. Two similar approaches were made to the problem. A recent study[2] has shown that organosilicon compounds which contain long-chained n-alkyl groups are quite thermally-stable and that such groups tend to lower the melting points of the organosilicon compounds into which they are incorporated. During the present study, it has been found that aralkyl groups, especially the gamma-phenylpropyl group, tend to give lower melting points than fully aromatic groups. Therefore, a large number of organosilicon monomers has been synthesized which contain n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, benzyl, β-phenylethyl and γ-phenylpropyl groups along with various combinations of other groups of known thermal stability. Since compounds which contain dissymetrical groups (m-tolyl, etc.) are known to melt, as a general rule, lower than compounds which contain more symmetrical groups (p-tolyl, etc.), another logical approach seemed to be the incorporation of such dissymmetrical groups into high-molecular weight organosilicon molecules. Accordingly, several such compounds were synthesized and studied.

Incidental to the preparation of these compounds, the synthesis of cyclohexyltriphenylsilane by a variety of methods has been studied. This preparation has been carried out because previous experimental work by others[3a] has shown that the compound can not be synthesized by two different

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[2]J. J. Goodman. Unpublished Ph. D. Thesis. Ames, Iowa, Iowa State College Library. 1955.

[3a]A. G. Brook and S. Wolffe, J. Am. Chem. Soc., 79, 1431 (1957).

procedures. The author has been able to prepare the compound in good yield by two methods, different from those tried earlier. Other procedures, including some similar to those tried previously[3a], have been found to give either little or no product resembling cyclohexyltriphenylsilane.

For the Historical part, a fairly complete review has been made of the organosilicon compounds which have been prepared and characterized in This Laboratory. In order to correlate the effect of various groups on the thermal stability, etc. of organosilicon compounds, the data gathered in this review have been compiled into several tables.

The broader literature has been reviewed from 1952 to May, 1957 for information about organosilicon compounds having groups similar to those incorporated into the organosilicon monomers prepared during this study.

HISTORICAL

As previously mentioned, the impetus to learn more about the chemistry of organosilicon compounds has been greatly accelerated, particularly during the past one and a half decades. As a result there is a need for frequent reviews of the advances which have been made in organosilicon chemistry to be compiled and published. Many excellent reviews[3b,4,5,6,7a,7b] have been prepared, but as the fund of information to be surveyed has increased, there has come a need for reviews which are more narrow in scope. An excellent example of this narrow type of review can be found in the recent compilation entitled "Carbon-functional Silicones[7b]."

Since the published reviews have included many compounds which are similar to the newly synthesized materials of the author, no attempt has been made to prepare an extensive literature survey. However, the literature has been reviewed from 1952 to May, 1957 for information about compounds containing groups similar to those incorporated into the

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[3b]C. A. Burkhard, E. G. Rochow, H. S. Booth and J. Hartt, Chem. Revs., 41, 97 (1947).

[4]H. W. Post, "Silicones and Other Organosilicon Compounds," Reinhold Publishing Corp., New York, N. Y., 1949.

[5]E. G. Rochow, "An Introduction to the Chemistry of the Silicones", John Wiley and Sons, Inc., New York, N. Y., 1951.

[6]H. Gilman and G. E. Dunn, Chem. Revs., 52, 77 (1953).

[7a]P. R. McGregor, "Silicones and Their Uses", McGraw-Hill Book Co., Inc., New York, N. Y., 1954.

[7b]P. D. George, M. Prober and J. R. Elliott, Chem. Revs., 56, 1065 (1956).

compounds prepared during the present study. This "Brief Survey of the Recent Literature" follows the first two sections of the Historical section which treat the compounds made in This Laboratory.

Organosilicon Compounds Prepared in This Laboratory

For the past several years This Laboratory has been active in the study of organosilicon chemistry. During this period over six hundred compounds (not all new ones, however) containing silicon have been prepared and characterized. A master alphabetical file (referred to later as the "master file") of all new compounds, including those containing silicon, has been maintained for a long period of time. However, no previous effort has been made to arrange into tables the data on organosilicon compounds found within this file. The information contained in the "file" is limited generally to the name of the compound, the name of the investigator who either prepared the compound or used it in his studies, and, in some cases, the melting point or boiling point of the compound. Since it was felt by the author that a rather complete compilation of data relating to compounds available for study as synthetic lubricants, hydraulic fluids or other purposes would be valuable, he has, by use of the "master file" and other sources described later, compiled sixteen tables in which the organosilicon compounds prepared in This Laboratory are listed along with some data which seemed to be of value. One of the prime objectives for preparing such tables was to enable correlations to be prepared which show the effect of various groups on such properties of organosilicon compounds as thermal stability, volatility and melting point and to apply these correlations in future research.

Division of the compounds into tables

The titles chosen for Tables 1 to 16 and the accompanying subheadings are as follows:

Table 1. Tetraalkylsilanes prepared in This Laboratory

A. R_4Si compounds

B. R_3SiR' compounds

C. $R_2SiR'_2$ compounds

Table 2. Trialkylarylsilanes prepared in This Laboratory

A. Trimethylarylsilanes

B. Other R_3SiAr compounds

Table 3. Dialkyldiarylsilanes prepared in This Laboratory

Table 4. Alkyltriarylsilanes prepared in This Laboratory

Table 5. Tetraarylsilanes prepared in This Laboratory

A. R_4Si compounds

B. Ph_3SiAr' compounds

C. $Ph_2SiAr'_2$ compounds

D. $PhSiAr'_3$ compounds

E. $ArSiAr'_3$ compounds

Table 6. Organosilicon derivatives of heterocyclic compounds prepared in This Laboratory

A. Dibenzofuran compounds

B. Thiophene and benzothiophene compounds

C. Dibenzothiophene compounds

D. 9-Ethylcarbazole compounds

E. Miscellaneous heterocyclic compounds

Table 7. Heterocyclic compounds prepared in This Laboratory in which silicon is an hetero atom

A. Dibenzosilole compounds

B. Phenoxasilin compounds

C. Phenothiasilin compounds

D. Spiro compounds

Table 8. Compounds prepared in This Laboratory which contain two or more silicon atoms bonded only to carbon

A. Compounds containing two silicon atoms separated by methylene or similar groups

B. Compounds containing two silicon atoms separated by a phenylene group

C. Compounds containing two silicon atoms separated by a biphenylene group

D. Compounds containing two p-(trimethylsilyl)-phenyl groups separated by one or more carbon atoms

E. Compounds containing two silicon atoms separated by an (oxydiphenylene) group

F. Compounds containing three silicon atoms

G. Compounds containing four or five silicon atoms

Table 9. Compounds prepared in This Laboratory which contain silicon-hydrogen bonds

A. R_3SiH compounds

B. $R_2R'SiH$ compounds

Table 10. Some compounds prepared in This Laboratory which contain silicon-halogen bonds

A. R_3SiX compounds

B. $R_2R'SiCl$ compounds

C. Miscellaneous chlorosilanes

Table 11. Compounds prepared in This Laboratory which contain silicon-hydroxyl bonds

A. R_3SiOH compounds

B. $R_2R'SiOH$ compounds

C. $R_2Si(OH)_2$ compounds

Table 12. Compounds prepared in This Laboratory which contain silicon-alkoxyl bonds

A. R_3SiOR' compounds

B. $R_2Si(OR')_2$ compounds

C. $RSi(OR')_3$ compounds

Table 13. Compounds prepared in This Laboratory which contain other Group IVB elements in addition to silicon and carbon

A. Compounds containing silicon and germanium

B. Compounds containing silicon and tin

C. Compounds containing silicon and lead

D. A compound containing silicon, germanium and tin

Table 14. Compounds prepared in This Laboratory which contain silicon to silicon bonds

A. R_3SiSiR_3 compounds

B. $R_xR'_{(6-x)}Si_2$ compounds

C. Compounds in which each of the silicon atoms present is within a cyclic group

D. Tri- and tetrasilanes

E. Disilanes containing H, Cl, OH and OR groups

Table 15. Compounds prepared in This Laboratory which contain silicon-oxygen-silicon linkages

A. R_6Si_2O compounds

B. $R_xR'_{(6-x)}Si_2O$ compounds

C. Compounds in which each of the silicon atoms is within a cyclic group

D. Miscellaneous groups

Table 16. Miscellaneous organosilicon compounds prepared in This Laboratory

A. Methanol derivatives

B. Acids, esters and salts

C. Mercapto, isocyanate and isothiocyanate compounds

D. $R_3SiNR'_2$ compounds

E. Miscellaneous nitrogen containing organosilicon compounds

The arrangement of the compounds within the various subheadings is somewhat arbitrary, but is as consistent as possible throughout the tables. The rules of arrangement which have been used are as follows:

1. Alkyl groups are listed before all other groups when such groups are possible within a subheading. Methyl groups precede other alkyl groups, followed by ethyl, etc.

2. Aralkyl groups are treated under the general heading of alkyl groups and follow the other alkyl groups, i.e., tetrabenzylsilanes follows tetra-n-octadecylsilane, etc.

3. Alicyclic and unsaturated groups just precede the saturated open-chained group(s) containing the same number of carbon atoms.

4. Aryl groups follow the aralkyl groups and within aryl groups, the phenyl group precedes the others followed by tolyl, naphthyl and biphenylyl. Within isomeric aryl groups, the order ortho, meta and then para is observed.

5. Groups which contain elements other than hydrogen and carbon are treated as derivatives of the corresponding hydrocarbon group and follow in the listing that group from which they may be considered to be derived, i.e., the m-(trifluromethyl)phenyl group follows the m-tolyl group, etc. Where several groups were found which might be considered to be derived from the same hydrocarbon group, the fluoro derivative is listed first followed by the chloro, bromo, hydroxyl, alkoxyl, mercapto, sulfonyl, amino, dialkylamino and then others.

6. Within some specific subheadings, there are only a few compounds and no particular order seemed necessary for such groups, i.e., see, for instance, Table 16, subheading A.

If the rules given above are used in connection with the table headings given previously, no difficulty should be encountered in locating compounds within a specific table.

Explanation of the columns in Tables 1-16

The tables are divided into several columns, and, since the source(s) of information for each of these columns is not the same, a brief description of each column and the way in which the data have been gathered follows:

Compound. The compound names appearing in this column have been obtained for the most part from the "master file" referred to earlier. However, some of them have been found by other means. The column entitled "Investigators" gives the identity of the source. See the discussion of the latter column for further information. When the original name found did not conform to the name recommended by Chemical Abstracts, the name recommended has been used.

M.p. or b.p. In this column is recorded, where available, the melting point in degrees Centigrade, or the boiling point (preceded by the abbreviations "lq." indicating that the compound is a liquid) in degrees Centigrade at some specific pressure in millimeters of mercury, i.e., the figures "127-128" should be read "m.p. 127-128° C", while "lq., 145-150/0.1" should be read "a liquid, b.p. 145-150° C at 0.1 mm. of mercury."

For most of the compounds, the information appearing in this column has been obtained from either printed articles or from theses. A few melting points have been found in the "master file" or in the Technical

Report described under the next subheading. For some compounds, no melting point or boiling point is recorded in any of the sources checked.

Thermal screening. Since several research projects to develop thermally-stable compounds have and are being conducted in This Laboratory, some method of obtaining a qualitative estimate of the thermal stability of the compounds is needed. For a very good measure of thermal stability, the isoteniscope method is available. However, the time required to complete such a study on each compound is prohibitive and a simpler method of evaluation has been adopted. This "Thermal screening" consists of simply heating a sample of the compound about the same size as that normally employed in taking melting points. The sample is placed in a capillary tube and then heated within a copper block using either a Tirrell burner or an electrical heating coil as a heat source. During the heating process a series of microbubbles is usually noted considerably below the volatilization point; this is believed to be an evolution of air trapped within the liquid, but may be a sign of decomposition. The temperature at which these microbubbles begin to form is usually recorded by the observer. The temperature at which the compound appears to volatilize is recorded as well as any evidence of decomposition.

Because much of the research on synthetic fluids is being financed by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, a Technical Report[8] has been prepared for

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[8]H. Gilman, R. K. Ingham and R. D. Gorsich, Wright Air Development Center Technical Report 53-426, Part I (January, 1954); H. Gilman and R. D. Gorsich, Wright Air Development Center Technical Report 53-426, Part II (January, 1955); Part III (January, 1956); Part IV (January, 1957). Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

them in four annual parts. In each of these parts are recorded, in tabular form, melting points and thermal screenings for some of the compounds which have been prepared for such studies. Most of the data appearing in the "Thermal screening" column has been taken from this Technical Report. Notation in the "References" column to "8-I" indicates that the data were taken from the first annual part of the Technical Report. Melting points from the Technical Report have served as checks against those obtained from other sources and in a few cases were the primary source of such data.

When the thermal screening data have been obtained from a source other than the Technical Report, or are not a personal observation of the author, an appropriate footnote has been made in the "Thermal screening" column. Because a detailed description of each thermal screening consumes much space, a series of abbreviations has been employed and these abbreviations are listed at the beginning of each table for the convenience of those using the tables.

Investigators. The names found in this column have been obtained for the most part by the use of the "master file" described previously. It is realized that reference to this "file" is in the realm of a private communication since the information is not readily available to the average reader. However, this file contains the most complete listing of organosilicon compounds prepared in This Laboratory and has been used with a full understanding of its nature. Most of the information taken from this "file" has been corroborated by data from other sources as may be noted by the presence of references, footnotes, etc. For any compound about which no information other than an investigator's name without a footnote is

given, no source of information other than the "master file" was found during this review.

Many of the investigators who are named in the tables have prepared Ph. D. or M. S. Theses in which organosilicon compounds are discussed. These works were not completely reviewed in the present study and more information about many of the compounds appearing in the tables may be obtained by consulting these Theses. For convenience, an alphabetical listing of the Theses has been incorporated (as References 75-95, page 104) into the "Bibliography on Organosilicon Compounds Prepared in This Laboratory" which follows Table 16. In the "Investigators" column, footnote "b" has been used to indicate that information on a compound (i.e., the compound in the same row of the table in which an investigator's name with footnote "b" is given) appears in the thesis of the investigator whose name is footnoted. In this column, footnote "c" has been used to indicate that some of the data within the table about a specific compound has been obtained by a private communication during 1957 from the person whose name is footnoted; footnote "c" has also been placed in the "Thermal screening" column to indicate that the thermal screenings so marked have been obtained by private communication.

References. This column of the tables contains a series of reference numerals which corresponds either to the Wright Air Development Center Technical Report (Reference 8) described earlier, or to the literature citations given as References 9-74 (pages 100-103) in the "Bibliography on Organosilicon Compounds Prepared in This Laboratory" which follows Table 16. Reference 12 in this series refers to this Dissertation; data

appearing in other theses are referred to in the previously described manner (see page 14). Most of the publications cited in References 9-74 have been submitted from This Laboratory and contain information regarding the preparations or reactions of compounds appearing in Tables 1-16. These publications have been carefully scanned for information relating to the compounds in the tables; where such information was found the corresponding reference numeral has been given in the "References" column.

The tables on organosilicon compounds follow in the order previously given:

Table 1. Tetraalkylsilanes prepared in This Laboratory[a,b,c].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res., residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., compound volatilizes
dec., decomposes or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
A. R_4Si compounds:				
Tetrakis(phenylthiomethyl)silane	67-69	mb. 300; vol. 368-370; lq. turns brn.	Cason	8-II, 14
Tetrakis(p-tolylthiomethyl)silane	70	mb. 280; vol. 365; turns or.	Cason	8-II, 14

[a]See pages 5-15 for a discussion of the tables; for information about each of the columns, see pages 11-15. It should be noted that all the compounds listed are not new and that the new compounds of the author are included in the tables.

[b]Wherever this footnote appears, more data about the compound can be found in the thesis of the investigator by whose name it appears. An alphabetical list of the Theses can be found (in References 75-95) beginning on page 104.

[c]Wherever this footnote appears, it should be interpreted to mean "private communication, 1957".

Table 1. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Tetra-n-octadecylsilane	50.0-50.5	mb. 330; vol. 464; no dec.	Ingham	8-I, 11
Tetrabenzylsilane	127-128	2 g. distilled at atm., b.p. 453-456; sl. bl.-brn. res., rmlt. 110-118	Ingham	8-I
Tetrakis(m-fluorobenzyl)-silane	62-63		Ingham	11
Tetrakis(β-phenylethyl)-silane	76.0-76.5	mb. 321; vol. 442-431; no dec.	Miles	8-II, 12, 13
Tetrakis(γ-phenylpropyl)-silane	lq., 230-240/ 0.1	mb. 220; sl. dec. 400; vol. 435-450	Miles	12, 13
B. R_3SiR' compounds (listed by character of R and then character of R'):				
Trimethyl-p-tolylthio-methylsilane	lq., 83-85/ 1.0		Cason	14
Benzyltrimethylsilane	lq., 93/35		Marshall[b], Clark[b]	15
Trimethyl-β-phenylethyl-silane	lq., 211°/atm.	mb. 160; vol. 175; no dec.	Marshall[b]	8-II, 15

Table 1. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
9-Fluorenyltrimethylsilane	96.0-96.5	mb. 280; vol. 320; no dec.	Illuminati, Benkeser[b], Miller Marshall	8-II, 16
Trimethyl(triphenylmethyl)silane	173-174	mb. 280; vol. 365; no dec.; rmlt. 172-174	Miller[b], Smith[b]	8-II, 17, 18
Triethylmethylsilane			Massie	19
Benzyltriethylsilane	lq., 250-252/atm.		Smith[b]	
Tris(2-cyclohexylethyl)-n-dodecylsilane	lq., 211/0.02		Meen	10
Tris(2-cyclohexylethyl)-n-octadecylsilane			Meen	
Cylohexyltri-n-dodecylsilane(attempted)			Miles	12
n-Butyltri-n-hexadecylsilane	lq., 260-263/0.001		Miles	12
Benzyltri-n-octadecylsilane	lq., 299-302/0.005		Miles	12, 13
Tribenzylcyclohexylsilane	lq., 198-200/0.25	some condensate at 400; vol. 420-435; no res. at 500.	Miles	12, 13

Table 1. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Tribenzyl-n-dodecylsilane	lq., 215-217/0.06	vol. 430-435; no res.[c]	Miles	12, 13
Tribenzyl-n-hexadecylsilane	lq.	yel. lq. vol. 425-430; no dec.	Gorsich[c]	8-II
Tribenzyl-n-octadecylsilane	lq., 235-240/0.04		Moore[c]	
Tris(m-fluorobenzyl)-n-hexadecylsilane	lq.	mb. 300; vol. 420; no dec.[c]	Lichtenwalter[c]	
n-Hexadecyltris(γ-phenylpropyl)silane	lq.	mb. 396; vol. 400; no dec.	Gorsich[c]	8-II
n-Octadecyltris(γ-phenylpropyl)silane	lq., 300-325/1.0		Moore[c]	
Benzyltris(γ-phenylpropyl)silane	lq., 214-217/0.04	mb. 280; vol. 420-430; no res.	Miles	12, 13
C. $R_2SiR'_2$ compounds;				
Di-n-dodecylbis(o-fluorobenzyl)silane[e]	lq., 222-226/0.005	mb. 350; vol. 421; sl. dec.[c]	Lichtenwalter[c]	

[e]These compounds were not analyzed because of the difficulty of obtaining true values due to volatilization of silicon dioxide as silicon tetrafluoride.

Table 1. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Di-n-dodecylbis(m-fluorobenzyl)silane[e]	lq., 130-140/ 0.005		Lichtenwalter[c]	
Di-n-dodecylbis(p-fluorobenzyl)silane	lq., 220-230/ 0.001		Lichtenwalter[c]	
Dibenzyldi-n-octadecylsilane	lq., 305-317/ 0.9	mb. 350; vol. 465-476; no res.	Miles	12
Bis(m-fluorobenzyl)di-n-octadecylsilane	lq., 300-310/ 0.04		Lichtenwalter[c]	
Di-n-octadecylbis(γ-phenylpropyl)silane	lq., 275-282/ 0.001	mb. 428; vol. 470-480; no res.; some dec. noted	Miles	12

Table 2. Trialkylmonoarylsilanes prepared in This Laboratory[a,b,c].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res. residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., compound volatilizes
dec., decomposes or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
A. Trimethylarylsilanes:				
Trimethylphenylsilane	lq., 172/atm.	vol. 170	Marshall[b], Dunn[b], Smith[b], Benkeser[b], Clark[b]	8-II
p-Chlorophenyltrimethylsilane	lq., 45-49/0.2		Marshall[b], Melvin[b]	
m-Bromophenyltrimethylsilane	lq., 60-65/0.03		Miles	
p-Bromophenyltrimethylsilane	lq., 53-56/0.1		Bullock, Melvin[b], Goodman, Benedict, Nobis[b], Clark[b]	20

[a,b,c]See footnotes a, b, and c, respectively, of Table 1, page 16.

Table 2. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
o-Methoxyphenyltrimethylsilane	lq., 205-206/atm.		Nobis[b]	21
p-Methoxyphenyltrimethylsilane	lq., 220/atm.		Marshall[b], Benkeser, Nobis[b]	21
N,N-Dimethyl-o-(trimethylsilyl)aniline	65.0-65.5		Sunthankar	22
m-(Trimethylsilyl)-aniline, acetyl and benzoyl derivatives	acetyl, 114-115° benzoyl, 121-125°		Summers[b]	
N,N-Dimethyl-m-(trimethylsilyl)aniline[d]	lq., 86-87/1.0		Sunthankar, Melvin[b]	20, 22
N,N-Bis(2-hydroxyethyl)-m-(trimethylsilyl)aniline	67-68		Sunthankar	23
p-(Trimethylsilyl)aniline	lq., 66/0.7		Benkeser[b]	
N,N-Dimethyl-p-(trimethylsilyl)aniline[d]	lq., 252-253/atm.		Melvin, Goodman Marshall[b]	15, 20

[d]The picrates of N,N-dimethyl-m- and p-(trimethylsilyl)aniline were prepared and both found to melt at 154-156°.

Table 2. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
p-Nitrophenyltrimethylsilane	lq., 82-83/0.7	mb. 210; vol. 237-240; no dec.	Sunthankar, Benkeser[b]	8-II
Trimethyl-p-tolylsilane	lq., 192/atm.		Marshall[b]	15
Note: The following 13 compounds are considered to be derived from trimethyl-p-tolylsilane.				
[p-(Chloromethyl)phenyl]-trimethylsilane			Bullock	
[p-(Chlorodiphenylmethyl)-phenyl] trimethylsilane			Miller	
p-(Trimethylsilyl)-benzyl alcohol[e]			Bullock	
[p-(Trimethylsilyl)-phenyl] phenylmethanol			Bullock	
[p-(Trimethylsilyl)-phenyl] diphenylmethanol			Bullock	
Benzyl[p-(trimethylsilyl)-phenyl]phenylmethanol			Bullock	

[e]The 3,5-dinitrobenzoate was also prepared, melting point was not given.

Table 2. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
2-[p-(Trimethylsilyl)-phenyl]ethanol[e]			Bullock	
[p-(Trimethylsilyl)-benzyl]phenyl ketone			Bullock	
p-(Trimethylsilyl)benz-aldehyde[f]	1q., 69-72/0.02		Melvin[b]	
p-(Trimethylsilyl)benzo-phenone[g]			Bullock	
p-(Trimethylsilyl)ben-zoyl chloride	1q., 74/0.2		Melvin[b]	
p-(Trimethylsilyl)ben-zoic acid	110-111°		Benedict, Bullock, Melvin[b]	
p-(Trimethylsilyl)-phenylacetic acid			Bullock	
Trimethyl-1-naphthyl silane	1q., 88/0.2	vol. 269	Dunn[b]	8-II, 16

[f]The 2,2-dinitrophenylhydrazone was prepared, m.p. 218-220.

[g]The oxime hydrochloride was also prepared.

Table 2. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	Reference[a]
1-Trimethylsilyl-2-naphthol	lq., 126-127/0.5		Sunthankar	24
(2-Methoxy-1-naphthyl)-trimethylsilane	lq., 108-109/0.4		Sunthankar	24
6-Trimethylsilyl-2-naphthol	107-108		Sunthankar	24
(1-Methoxy-2-naphthyl)-trimethylsilane	lq., 99-100/0.4		Sunthankar	24
(3-Methoxy-2-naphthyl)-trimethylsilane	59		Sunthankar	24
(6-Methoxy-2-naphthyl)-trimethylsilane	77-78		Sunthankar	24
2-Biphenylyltrimethylsilane	lq., 97-102/0.06		Goodman[b]	
3-Biphenylyltrimethylsilane	lq., 170/20	vol. 300; no dec. 8-II	Lichtenwalter	8-II, 25
B. Other R_3SiAr compounds:				
Triethylphenylsilane	lq., 71-72°/0.45		Smith[b], Benkeser[b]	

Table 2. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Triethyl-p-methoxyphenylsilane	lq., 103/0.2	vol. 264; no dec.	Benkeser[b]	8-I, 16
3-(Triethylsilyl)-6-methoxybenzoic acid	52-56		Benkeser[b]	
Triethyl-p-tolylsilane	lq.	vol. 247-252; no dec.	Benkeser[b]	8-I
Triallylphenylsilane	lq., 90-92/0.8		Meen	10
Triisopropylphenylsilane	lq., 90-91/4	vol. 259	Clark	8-II, 26
Tri-n-butylphenylsilane	lq., 116-118/0.9	mb. 270; vol. 299; no dec.[c]	Marshall[b], Miles	12, 15
2-Biphenylyltri-n-butylsilane (attempted)			Miles	12
Tri-n-hexylphenylsilane[h]		turns brn, 380; vol. 380; brn. lq. res.		8-II
Tris(2-cyclohexylethyl)-phenylsilane	lq., 188/0.02		Meen	10

[h]This compound is reported in Reference 8-II, but no other information was found for the compound.

Table 2. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Tri-n-octylphenylsilane	lq., 181/0.02		Meen	10
Tris(2-ethylhexyl)phenylsilane	lq., 156-157/0.03		Meen	10
2-Biphenylyltri-n-decylsilane	lq., 235-238/0.001	mb. 360; vol. 430-440; sl. res. at 490	Miles	12
Tri-n-dodecylphenylsilane	lq., 230-240/0.001	mb. 330; vol. 430; no res.	Miles, Cason[i,b]	12
2-Biphenylyltri-n-dodecylsilane	lq., 245-247/0.005	mb. 320; vol. 470-480; condensate is am., no res.	Miles	12
Tri-n-tetradecylphenylsilane	lq., 278-283/0.02		Moore[c]	
(p-Chlorophenyl)tri-n-hexadecylsilane	lq., 295-300/0.005	mb. 400; vol. 452-460; sl. brn. res. at 520	Miles	12
Tri-n-hexadecyl-p-phenoxyphenylsilane	lq., 315/0.005	mb. 410; vol. 440-450	Miles	12

[i]The attempted preparation of this compound by Cason was unsuccessful.

Table 2. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
2-Biphenylyltri-n-hexadecylsilane	lq., 270/0.001	mb. 380; vol. 440-450; sl. res.	Miles	12
4-Biphenylyltri-n-hexadecylsilane	lq., 321-323/0.002 mm.	mb. 340; vol. 450-460; sl. brn. res. at 500	Miles	12
Tribenzylphenylsilane	59-60	mb. 400; vol. 448-450; no dec.	Miles	8-I, 12, 13, 27
Tribenzyl-p-methoxyphenylsilane	83-85	mb. 260; vol. 445-455; sl. bl. res.	Marshall[b]	8-I, 15
Tribenzyl-3-biphenylylsilane	133-144	mb. 410; vol. 492-500[c]	Trepka[c]	
Phenyltris(β-phenylethyl)silane	62.0-62.7	mb. 340; vol. 430-440; no res.	Miles	12, 13
Phenyltris(γ-phenylpropyl)silane	59.5-60.0	mb. 298; vol. 420-426; condensate is yel.	Miles	8-I, 12, 13
Tri-9-fluorenylphenylsilane	149-150(corr.)	mb. 340; ot. vol. 380; vol. 410; r. res.	Goodman[b]	8-II, 28

Table 3. Dialkyldiarylsilanes prepared in This Laboratory[a,b,c].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res., residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., compound volatilizes
dec., decomposes or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Bis(p-chlorophenyl)dimethylsilane	47		Miller[b]	29
Diethyldiphenylsilane	lq.	mb. 280; vol. 298-300; no dec.	Marshall[b]	8-II, 15
Diallyldiphenylsilane	lq., 128-120/atm.		Meen	10
Bis(2-cyclohexylethyl)-diphenylsilane	lq., 187/0.03		Meen	10
Di-n-octyldiphenylsilane	lq., 198/0.02		Meen	10

[a,b,c]See footnotes a, b, and c, respectively, of Table 1, page 16.

Table 3. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Di-2-octyldiphenylsilane	lq., 186/0.5		Meen	10
Bis(2-ethylhexyl)diphenylsilane	lq., 158-159/0.06		Meen	10
Di-10-hendecenyldiphenylsilane	lq., 258-260/0.15		Ingham	11
Di-n-hendecyldiphenylsilane	lq., 262-262/0.1	mb. 210; vol. 400-440	Ingham	8-II, 11
Di-n-dodecyldiphenylsilane	lq., 225-231/0.015	mb. 270; vol. 439-443; no dec.	Moore[c]	8-II
Di-n-dodecylbis(m-fluorophenyl)silane	lq., 240-250/0.001	mb. 400; vol. 455-470; brn. res. at 520	Miles	12
Bis(m-chlorophenyl)di-n-dodecylsilane	lq., 260-270/0.008	mb. 350; vol. 420-430; bl. res. 450	Miles	12
Bis(p-chlorophenyl)di-n-dodecylsilane	lq., 275-280/0.005	vol. 420-430; much res. on tube wall	Miles	12
Di-n-dodecylbis(o-phenoxyphenyl)silane	lq., 260-270/0.001	mb. 370; vol. 460-470; no res.	Miles	12
Di-n-dodecylbis(p-phenoxyphenyl)silane	lq., 275-280/0.001	mb. 400; vol. 450-470; no res.; condensate was brn.	Miles	12

Table 3. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal Screening[a]	Investigators[a]	References[a]
Di-n-octadecyldi-p-tolylsilane	ca. 35°; very waxy	mb. 400; vol. 430-445; no res. 500	Miles	12
Dibenzyldiphenylsilane	61.0-61.6	mb. 300; vol. 432; no dec.	Miles	8-I, 12, 13 27
Diphenylbis(β-phenylethyl)silane	74.0-74.5	mb. 340; vol. 425-440; no res.	Miles	8-I, 12, 13
Diphenylbis(γ-phenylpropyl)silane	lq., 252-253/0.04	mb. 284; vol. 416-420; brn. condensate	Miles	8-II, 12, 13
Di-9-fluorenyldiphenylsilane	270-271	mb. 420; vol. 440; r. res.	Goodman[b]	8-II, 28

Table 4. Alkyltriarylsilanes prepared in This Laboratory[a,b,c].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res., residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., compound volatilizes
dec., decomposes, or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Methyltriphenylsilane	66-67	mb. 270; vol. 300; no dec.	Melvin[b], Nobis[b], Smith[b], Miller, Clark[b]	8-II, 30
Tris(p-chlorophenyl)-methylsilane	86		Miller[b]	29
Tris(p-chlorophenyl)-trichloromethylsilane	161		Miller[b]	29
Triphenyl(trichloromethyl)-silane	194		Miller[b]	29
Triphenylsilylmethanol	116-118		Brook, Wu	31

[a,b,c]See footnotes a, b, and c, respectively, of Table 1, page 16.

Table 4. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Triphenyl(p-tolylthiomethyl)silane	148-149		Cason	14
(Methylsulfonylmethyl)triphenylsilane	177.0-178.5	amb. lq. 330-340; mb. 340; bub. 360; pt. vol. 360-390; bl. 390; bl. res. 520	Miles	12
Triphenyl(p-tolylsulfonylmethyl)silane	173-174		Cason	14
Ethyltriphenylsilane	74.5-76.5°		Marshall[b], Nobis[b]	
(1-Chloroethyl)triphenylsilane	129-130		Nobis[b]	21
(2-Chloroethyl)triphenylsilane	124-125		Nobis[b]	21
Triphenyl[2-(phenylthio)ethyl]silane	99-100		Cason[d]	14
S,S-Dioxide of previous compound	155		Cason[d]	14

[d]These compounds were apparently prepared in the Laboratories of Tuskegee Institute, although some of the compounds in Reference 14 were prepared in This Laboratory.

Table 4. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
[2-(Benzylthio)ethyl]-triphenylsilane	72-73		Cason[d]	14
S,S-Dioxide of previous compound	153-154		Cason[d]	14
Triphenyl[2-(p-tolylthio)ethyl]silane	97-99		Cason[d]	14
S,S-Dioxide of previous compound	152		Cason[d]	14
Allyltriphenylsilane			Meen	
Triphenyl-n-propylsilane	84	mb. 260; vol. 365; no dec.	Miller[b]	8-I, 17
n-Butyltriphenylsilane	87.5-88.0	mb. 330; vol. ca. 380; no dec.	Melvin[b], Dunn, Hartzfeld, Miller, Sunthankar	8-I, 16, 30
n-Butyltri-1-naphthylsilane	189-190		Brannen[b]	32
Cyclopentyltriphenylsilane	110-111	mb. 225; vol. 400-410; condensate is bl.-brn.	Gorsich[c]	8-II

Table 4. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	Reference[a]
4-Pentenyltriphenylsilane	45.2-46.4	mb. 300; vol. 418-430; brn. lq. res. at 440	Gorsich[c]	8-II
n-Amyltriphenylsilane	47	mb. 270; sl. milky after melting; vol. 390	Miller[b]	8-I, 17
Cyclohexyltriphenylsilane	147-148	mb. 350; vol. 420-425; no res.	Miles	12
n-Hexyltriphenylsilane	78	mb. 320; vol. 399-402; no dec.; rmlt. 78	Miller[b]	8-I, 17
(2-Cyclohexylethyl)triphenylsilane	58-59		Meen	10
n-Octyltriphenylsilane	73-75		Meen	10
2-Octyltriphenylsilane	lq., 153-155/0.04		Meen	10
(2-Ethylhexyl)triphenylsilane	lq., 163-166/0.03		Meen	10
n-Decyltriphenylsilane	68.0-68.5	mb. 320; lq. yel. 400; vol. 442-445	Gerow, Miles	8-I, 10
n-Dodecyltriphenylsilane	67.5-68.0	mb. 320; lq. lt. yel. 400; vol. 440-445	Merten	8-I, 33

Table 4. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
n-Dodecyltris(m-fluorophenyl)silane		mb. 370; vol. 410-420; res. on capillary wall	Gorsich[c]	8-II
Tris(m-chlorophenyl)-n-dodecylsilane		mb. 390; vol. 425-435; condensate lt. or.	Gaj[c]	8-III
Tris(p-chlorophenyl)-n-dodecylsilane	lq., 240/0.1	mb. 360; vol. 435-445; condensate is discolored	Gaj[c], Miller[b]	8-II, 8-III, 29
n-Dodecyltris(p-phenoxyphenyl)silane	lq., 315-320/0.004 in an Hickman still	mb. 420; vol. 450-460; res. is am.	Goodman[b]	8-II, 28
n-Dodecyltri-m-tolylsilane	lq., 200-206/0.001; lq. freezes to a glass at -28	mb. 300; vol. 430-440; no dec. noted	Miles	8-IV, 12
Tri-2-biphenylyl-n-dodecylsilane	lq., 295/0.08		Oita[b]	
Tri-3-biphenylyl-n-dodecylsilane	lq., 310-315/0.01	mb. 390; vol. 480; no dec.	Lichtenwalter	8-IV, 25
Triphenyl-n-tetradecylsilane	66-67		Merten	33

Table 4. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
n-Hexadecyltriphenylsilane	68.5-69.0		Merten	33
Tris(m-fluorophenyl)-n-hexadecylsilane	36-38	mb. 370; vol. 410-420; res. on capillary wall	Gorsich[c]	8-II
Tris(m-chlorophenyl)-n-hexadecylsilane	lq.	sl. darkening 360; vol. 425-435 with more darkening	Gaj[c]	8-III
Tris(p-chlorophenyl)-n-hexadecylsilane	lq.	vol. 440-450; no dec.	Gaj[c]	8-III
n-Heptadecyltriphenylsilane	71.0-71.5		Merten	33
n-Octadecyltriphenylsilane	78-79 72-73	mb. 320; p. yel. 400; vol. 442-445	Merten	8-I, 33
Tris(m-fluorophenyl)-n-octadecylsilane	38-39	mb. 370; vol. 410-420; res. on capillary wall	Gorsich[c]	8-II
Tris(m-chlorophenyl)-n-octadecylsilane		darkens 410; vol. 435 with dec.	Gaj[c]	8-III
Tris(p-chlorophenyl)-n-octadecylsilane		vol. 450-460; sl. dec.	Gaj[c]	8-III

Table 4. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Tri-2-biphenylyl-n-octadecylsilane		mb. 400; vol. 420-470; clear lq. res.; no dec.	Oita[b]	8-III
Tri-3-biphenylyl-n-octadecylsilane	lq.	mb. 320; vol. 470 with dec.	Lichtenwalter	8-IV, 25
Benzyltriphenylsilane	91-92, 98-99	mb. 330; vol. 432; no dec.	Miller[b], Wu[b], Melvin[b]	8-I, 17, 34, 35
1-Indenyltriphenylsilane	136	mb. 380; milky 400; vol. 430; no res.	Miller[b]	8-II, 17
Triphenyl(phenylethynyl)-silane	98-99	yel. 350; mb. 370; vol. 445-460; r.-brn. res.	Plunkett[b], Nobis[b], Melvin, Miller[b]	8-II, 17, 34
Triphenylstyrylsilane	144-146, 146-147	mb. 190; yel. 350; tan 440; vol. 445-470	Nobis[b]	8-II, 21
Triphenyl(β-phenylethyl)-silane	147	mb. 356; vol. 428; no dec. rmlt. 144-145	Miller[b], Miles	8-I, 12, 13 17
Triphenyl(γ-phenylpropyl)-silane	62.5-64.0	mb. 270; darkens 400; vol. 435-442	Miles	12, 13
(Diphenylmethyl)triphenyl-silane	159		Miller[b]	17

Table 4. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
9-Fluorenyltriphenyl-silane	183-184	mb. 280; pt. vol. 455-460; vol. 500; r. lq. at 480	Miller[b] Goodman[b]	8-II, 17
Triphenyl(β,β diphenyl-ethyl)silane	106-108	mb. 340; vol. 420-432; no dec.		8-I
Triphenyl(α,β-diphenyl-ethyl)silane	135-136	mb. 370; vol. 390; no dec.	Wu	8-I, 36
Triphenyl(1,2,3,4-tetra-phenylbutyl)silane	155-157		Tai, Brook	37
Triphenyl(triphenyl-methyl)silane	334-336		Brook, Benkeser	38
Triphenyl-9-(9-phenyl-fluorenyl)silane			Hartzfeld	

Table 5. Tetraarylsilanes prepared in This Laboratory[a,b,c].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res., residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., compound volatilizes
dec., decomposes, or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
A. Ar_4Si compounds:				
Tetraphenylsilane[d]	232-233	mb. 260; bub. 400; vol. 420-425; no dec.	Wu[b], Clark[b], etc.	8-I
Tetrakis(m-fluorophenyl)-silane	195-197	mb. 350; vol. 394; no dec.; rmlt. 196-198	Gorsich[c]	8-II
Tetrakis(m-chlorophenyl)-silane	148.0-148.9	mb. 320; vol. 472; no dec.; sl. brn. res.	Gorsich[c]	8-II

[a,b,c]See footnotes a, b, and c, respectively, of Table 1, page 16.

[d]Tetraphenylsilane has been reported by almost every investigator who has studied organosilicon compounds in This Laboratory.

Table 5. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Tetrakis(p-chlorophenyl)-silane	181	mb. 310; yel. 400; vol. 494-496	Miller[b]	8-II, 29
Tetrakis(o-methoxy-phenyl)silane	224.0-224.5		Smart	39
Tetrakis(o-phenoxy-phenyl)silane	284-285	vol. 540; no dec. below 570	Oita	8-III, 40
Tetrakis(p-phenoxy-phenyl)silane	204,206	no noticable vol. below 510; no dec.	Goodman[b]	8-II, 28
Tetrakis[p-(dimethylamino)-phenyl]silane	234-235°		Plunkett[b], Dunn[b]	46
Tetra-o-tolylsilane[e]	145, 228, 300, 344 and possibly 270		Smart	41
Tetra-m-tolylsilane	155-156	vol. 435; some dec.	Goodman[b]	8-IV, 28
Tetrakis[m-(trifluoro-methyl)phenyl]silane	102-103	mb. 340-350; vol. 340-360; condensate is am.	Goodman[b]	8-II, 28

[e]There are several stereoisomeric tetra-o-tolylsilanes prepared by either Dr. Smart, now of Muhlenberg College, Pa., or by his co-worker, H. W. Otto.

Table 5. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Tetra-p-tolylsilane	227-230	mb. 370; vol. 452; no dec.	Benedict, Dunn[b], Brook, etc.	8-I, 42
Tetra-2-naphthylsilane	215-216	mb. 280; brn. 460; r.-brn. 450; vol. 565-570	Brannen[b]	8-I, 43
Tetra-3-biphenylylsilane	137.0-137.5	mb. 550; vol. 570; no dec.	Lichtenwalter	8-IV, 25
B. Ph_3SiAr compounds:				
(m-Fluorophenyl)triphenylsilane	208-209	mb. 364; vol. 412; no dec.; rmlt. 208-210	Gorsich[c]	8-II
(p-Fluorophenyl)triphenylsilane	183.1-184.4	mb. 220; vol. 414-424	Gorsich[c]	8-II
(m-Chlorophenyl)triphenylsilane	157-158	mb. 320; vol. 442-452; brn. res.	Gorsich[c]	8-II
(p-Chlorophenyl)triphenylsilane	157	mb. 380; vol. 440-446; no dec.	Miller[b]	8-III, 29
(p-Bromophenyl)triphenylsilane	167-168	mb. 370; lq. yel. 450; vol. 458-462	Melvin[b], Eisch, Oita	8-I, 44

Table 5. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
2-(Triphenylsilyl)phenol	236-239		Melvin[b], Oita	45
4-(Triphenylsilyl)phenol	225-227	mb. 340; vol. 403; no dec.	Melvin[b], Brannen	8-I
(p-Methoxyphenyl)triphenylsilane	158-160	mb. 250; vol. 440-445; no dec.	Marshall[b], Benkeser[b], Plunkett	8-I
[o-(2-Phenoxyethoxy)phenyl]triphenylsilane	112.0-113.5	vol. 430-440; o. condensate	Oita	8-III, 40
(o-Phenoxyphenyl)triphenylsilane	143-145	vol. 450; all by 480; no res.	Oita	8-III, 40
(2-Phenoxy-5-chlorophenyl)triphenylsilane	163.0-163.5	vol. 450; no dec.	Oita	8-III, 40
N,N-Dimethyl-o-(triphenylsilyl)aniline	95.5		Sunthankar	22
m-(Triphenylsilyl)aniline	248-251		Summers[b]	
N,N-Dimethyl-m-(triphenylsilyl)aniline[f]	95-96		Melvin[b]	44

[f]The hydrochloride melts at 210-211.

Table 5. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
N,N-Dimethyl-p-(triphenylsilyl)aniline[g]	144-146	mb. 240; vol. 440; no dec.	Marshall[b], Plunkett[b]	8-II, 46
N,N-Bis(2-hydroxyethyl)-m-(triphenylsilyl)aniline	oily solid		Sunthankar	23
2,5-Dimethyl-1-[p-(triphenylsilyl)phenyl]-pyrrole	187.5-188.5	mb. 250; brn. 250; dec. slowly above 270; condensate is dark	Benkeser[b], Melvin[b]	8-II
Triphenyl-o-tolylsilane	188-190; 186.5-187.5		Wu[b], Smart	35, 39
Triphenyl-m-tolylsilane	150-151	vol. 430; sl. dec.	Goodman[b]	8-IV, 28
[m-(Trifluoromethyl)-phenyl]triphenylsilane	101, 91-92	mb. 325; vol. 400; no dec.	Miller[b], Goodman[b]	8-I, 29
Triphenyl-p-tolylsilane	138-140; 140-141	mb. 385; vol. 430; no dec.	Brannen[b], Clark[b], Wu[b], Benedict, etc.	8-I, 35, 42, 48
Note: The following 9 compounds are considered to be derived from triphenyl-p-tolylsilane.				
Triphenyl[p-(diphenylmethyl)phenyl]silane	214-216		Brook	38

[g]The hydrochloride melts at 227-229.

Table 5. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Triphenyl[p-(dichloromethyl)phenyl] silane	171.5-173.5°		Marshall[b]	
Triphenyl[p-(bromomethyl)phenyl] silane	170-171	yel. on melting; darkens and vol. 290; bl. 290	Brannen[b]	8-I, 49
Triphenyl[p-(dibromomethyl)phenyl] silane	184.0-184.5	yel. on melting; vol. and darkens 325	Brannen[b]	8-I, 49
p-(Triphenylsilyl)benzyl cyanide			Brannen	
p-(Triphenylsilyl)benzyl alcohol	54-55		Brannen[b]	49
Diphenyl[p-(triphenylsilyl)phenyl] methanol			Miller	
p-(Triphenylsilyl)benzaldehyde	110-111[h]		Brannen[b]	49
p-(Triphenylsilyl)benzoic acid	213-214		Brannen[b], Wu[b]	49

[h]The oxime melts at 194-195, and the thiosemicarbazone at 234-235.

Table 5. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
1-Naphthyltriphenylsilane	172-175.5	mb. 320; vol. 472-474; no dec.	Brannen[b]	8-I, 32
1-Triphenylsilyl-2-naphthol[i]			Sunthankar	
(2-Methoxynaphthyl)-triphenylsilane	165-166		Sunthankar	24
2-Naphthyltriphenyl-silane	138-140[j] 150-151	mb. 360; yel. 470; vol. 490; no dec.	Brannen[b]	8-I, 47
6-Triphenylsilyl-2-naphthol	139-140		Sunthankar	24
(1-Methoxynaphthyl)-triphenylsilane	176-177		Sunthankar	24
(3-Methoxynaphthyl)-triphenylsilane	131-132		Sunthankar	24
(6-Methoxynaphthyl)-triphenylsilane	168		Sunthankar	24

[i]This compound was not rigorously identified.

[j]The melting point of 138-140 for 2-naphthyltriphenylsilane was reported in the first annual report to the Air Force.[8] The compound screened may possibly been 6-triphenylsilyl-2-naphthol, m.p. 139-140.

Table 5. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
2-Biphenylyltriphenylsilane	136-137	vol. 450-480; brn. res. to above 510	Oita	8-II, 50
2-(2'-Chlorobiphenylyl)-triphenylsilane	157-158	mb. 270; vol. 480-490; condensate yel., res. o.	Gorsich[c]	8-III
2-(2'-Bromobiphenylyl)-triphenylsilane	152.5-154.0	mb. 300; brn. 430; vol. 480-490; res. brn.	Gorsich[c]	8-II
3-Biphenylyltriphenylsilane	128-129	mb. 320; vol. 480; no dec.	Lichtenwalter	8-IV, 25
C. $Ph_2SiAr'_2$ compounds:				
Bis(m-fluorophenyl)diphenylsilane	195.0-195.8	mb. 390; vol. 404-408; no dec.; rmlt. 196-197.5	Gorsich[c]	8-II
Bis(m-chlorophenyl)diphenylsilane	110-111	mb. 380; vol. 442-448; sl. yel. condensate	Gorsich[c]	8-II
Bis(p-chlorophenyl)diphenylsilane	131	mb. 240; vol. 455-465; sl. p.-brn. res.	Dunn, Miller[b]	8-II, 29
2,2'-(Diphenylsilylene)-bis-(phenol)	206-207	vol. 300; condensate yel.; res. glassy at 400	Oita	8-III, 45

Table 5. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Bis[o-(2-phenoxyethoxy)-phenyl] diphenylsilane (impure)			Oita	
Bis(o-phenoxyphenyl)di-phenylsilane	164-165	vol. 470; res. is dark at 500	Oita	8-III, 40
Bis(2-phenoxy-5-chloro-phenyl)diphenylsilane	151-152	vol. 500-510; no dec.	Oita	8-III, 40
Bis(p-phenoxyphenyl)di-phenylsilane	162-163	pt. vol. 400; p. am. lq. 475; vol. 505	Goodman[b]	8-II, 28
4,4'(Diphenylsilylene)-bis[N,N-dimethylaniline]	180-181		Plunkett[b]	46
Diphenyldi-o-tolylsilane	174.0-174.2		Smart	39
Diphenyldi-m-tolylsilane	119-120	mb. 119-120; vol. 435; sl. dec.	Goodman[b]	8-IV, 28
Bis[m-(trifluoromethyl)-phenyl] diphenylsilane	96-97	pt. vol. 320-340; vol. 375-380	Goodman[b]	8-II, 28
Diphenyldi-p-tolylsilane	121-122[k], 118-119	mb. 375; vol. ca. 400; no dec.	Brannen[b], Clark	8-I, 47, 48

[k]Clark reported a melting point of 176-177. This melting point was shown in Reference 47 to be a possible melting point of a 1:1 mixture of tetra-p-tolyl- and tetraphenylsilane.

Table 5. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Di-1-naphthyldiphenylsilane	194-195 (corr.)		Brannen[b]	32
Di-2-biphenylyldiphenylsilane	137.0-137.5	yel. 480; vol. 490-520; brn. res. 530-550	Oita	8-II, 50
Di-3-biphenylyldiphenylsilane	134.5-135.0	vol. 520; sl. dec.	Lichtenwalter	8-II, 25
D. $PhSiAr'_3$ compounds:				
Tris(m-fluorophenyl)-phenylsilane	191.5-193.0	mb. 346; vol. 402; no dec.; rmlt. 191-192	Gorsich[c]	8-II
Tris(m-chlorophenyl)-phenylsilane	87.5-88.8	mb. 240; vol. 462 no dec.	Gorsich[c]	8-II
Tris(p-chlorophenyl)-phenylsilane	134	mb. 300; yel. 400; vol. 480-485	Miller[b]	8-II, 29
Tris(o-phenoxyphenyl)-phenylsilane	192-193	vol. 510; sl. dec. on wall of capillary; sl. res.	Oita	8-III, 40
Tris(p-phenoxyphenyl)-phenylsilane	149-150	p. am. 420; am. 460; vol. above 510	Goodman[b]	8-II, 28

Table 5. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
4,4',4"-(Phenylsilyl-idyne)tris[N,N-dimethyl-aniline]	171-173		Plunkett[b]	46
Phenyltri-o-tolylsilane	195.5-195.9		Smart	39
Phenyltri-m-tolylsilane	128-129	vol. 420-425; lq. am. before vol.	Goodman[b]	8-IV, 28
Tris[m-(trifluoromethyl)-phenyl] phenylsilane	80-81	mb. 330; vol. 365-370; am. res.	Goodman[b]	8-II, 28
Phenyltri-p-tolylsilane	182-183,[1] 127-128	mb. 374; vol. ca. 445; no dec.	Clark[b], Brook, Brannen[b]	8-I, 47, 51
Tri-1-naphthylphenyl-silane	192-193	mb. 280; yel. 450; brn. 525; vol. 533-540, res.	Brannen[b]	8-I, 47
Tri-2-biphenylylphenyl-silane	184	yel. on melting; pt. vol. 460; vol. 500 with darkening; yel. res.	Oita	8-II, 50
Tri-3-biphenylylphenyl-silane	amorphous	mb. 320; vol. 548; no dec.	Lichtenwalter	8-IV, 25

[1]The m.p. of 127-128 was reported by Clark, doctoral dissertation, Iowa State College, 1956. See Reference 47 for further information.

Table 5. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
E. $ArSiAr'_3$ compounds, Ar or Ar' are not phenyl groups:				
(p-Bromophenyl)tri-o-tolylsilane			Brannen[b]	
(p-Methoxyphenyl)tri-(o-methoxyphenyl)silane	178-180		Smart	39
4,4',4"(p-Methoxyphenylsilylidyne)tris[N,N-dimethylaniline]	118-119	mb. 230; vol. 435-440	Plunkett	8-II
(p-Methoxyphenyl)tri-o-tolylsilane	179-180	yel. 420; mb. 450; darkens 460; vol. 500; brn. res.	Smart	8-II, 39
Tri(o-methoxyphenyl)-o-tolylsilane	193.5-194.0		Smart	39
Tri-1-naphthyl-p-tolylsilane	232-233	mb. 320; yel. 470; r. 530; vol. 530-533	Brannen[b]	8-I, 47

Table 6. Organosilicon derivatives of heterocyclic compounds prepared in This Laboratory[a,b,c].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res., residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., compound volatilizes
dec., decomposes, or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
A. Dibenzofuran compounds:				
2-(Triphenylsilyl)dibenzofuran	137.5-138.5		Meen, Nobis[b]	21, 52
4-(Triphenylsilyl)dibenzofuran	153-154		Meen, Nobis[b]	52
B. Thiophene and benzothiophene compounds:				
2-(Trimethylsilyl)-thiophene	lq., 161-163/ atm.		Marshall[b]	

[a,b,c]See footnotes a, b, and c, respectively, of Table 1, page 16.

Table 6. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
2-(Triphenylsilyl)-thiophene	196-198	mb. 280; vol. 420; no dec.	Marshall[b], Benkeser[b], Plunkett[b]	8-I, 16
5-(Triphenylsilyl)-2-thiophenecarboxylic acid	188-190		Benkeser[b]	16
2-[5-(Triphenylsilyl)-2-thienyl] quinoline	168-170		Plunkett[b]	53
4,7-Dichloro-2-[5-(triphenylsilyl)-2-thienyl]-quinoline	200-203		Plunkett[b]	53
6-Methoxy-2-[5-(triphenylsilyl)-2-thienyl]-quinoline	227-228		Plunkett[b]	53
2-(Triphenylsilyl)-Benzothiophene	148-149		Meen	52
C. Dibenzothiophene compounds:				
1-(Trimethylsilyl)dibenzothiophene	lq., 150-155/0.25		Wilder	
1-(Trimethylsilyl)dibenzothiophene-5,5-dioxide			Wilder	

Table 6. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
2-(Trimethylsilyl)dibenzothiophene	48.2-49.2		Illuminati	54
2-(Trimethylsilyl)dibenzothiophene-5,5-dioxide	164-165	mb. 360; yel. 400; vol. 425; no dec.	Illuminati	8-I, 54
3-(Trimethylsilyl)dibenzothiophene	103.5-104.5	mb. 240; vol. 362-364; no dec.	Illuminati	8-I, 54
3-(Trimethylsilyl)dibenzothiophene-5,5-dioxide	172-174; 170.8-171.8	mb. 210; yel. 400; vol. 427; no dec.	Illuminati	8-I, 54
4-(Trimethylsilyl)dibenzothiophene	lq., 215-217/20		Summers, Nobis[b]	21
4-(Trimethylsilyl)dibenzothiophene-5,5-dioxide	146-147	mb. 358; vol. 412-420; condensate was yel.	Summers, Nobis[b]	8-II, 21
3(?)-Nitro-4-(trimethylsilyl)dibenzothiophene-5-dioxide	223-224	or. on melting; mb. 238; dec. 351; brn. res.	Nobis[b]	8-II, 21
2-(Triphenylsilyl)-dibenzothiophene	153-154		Meen	52

Table 6. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
4-(Triphenylsilyl)dibenzothiophene	196-198,[d] 193-194 189-192	mb. 270; bl. at 485; vol. 535-540; bl. res.	Meen, Nobis[b]	8-I,21, 52
4-(Triphenylsilyl)dibenzothiophene-5,5-dioxide	212-213		Nobis[b]	21
D. 9-Ethylcarbazole compounds:				
1-(Triphenylsilyl)-9-ethylcarbazole	187-198		Meen	52
3-(Triphenylsilyl)-9-ethylcarbazole	218-220		Meen	52
6-Chloro-3-(triphenylsilyl)-9-ethylcarbazole	166-168		Meen	52
3,3'(Diphenylsilylene)-bis[9-ethylcarbazole]	233-235		Meen	52
3,3',3"(Phenylsilylidyne)tris[9-ethylcarbazole]	292-294		Meen	52

[d]The lowest melting point is reported in Reference 8-I, the highest one in Reference 52 and the intermediate one in Reference 21.

Table 6. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Tetrakis[3-(9-ethyl-carazolyl)]silane	335-337		Meen	52
E. Miscellaneous heterocyclic compounds:				
2-(Triphenylsilyl)-Benzothiazole	141-142		Meen	52
1-(Triphenylsilyl)-thianthrene	190.0-191.5		Swayampati	55
Tetrakis(2-benzoxazolyl) silane			Bullock	

Table 7. Heterocyclic compounds prepared in This Laboratory in which silicon is an hetero atom[a,b,c].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res., residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., compound volatilizes
dec., decomposes, or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
A. Dibenzosilole compounds:[d]				
5,5-Diethyldibenzosilole	61-62	mb. 266; vol. 315-320; no dec.; rmlt. 61-62	Gorsich[c]	8-III
5-[(Dibenzylmethylsilyl)methyl]-5-n-dodecyldibenzosilole		mb. 400; vol. 440-450; then 460; yel. condensate	Gorsich[c]	8-IV

[a,b,c]See footnotes a, b, and c, respectively, of Table 1, page 16.

[d]The names "dibenzosilole, phenoxasilin, and phenothiasilin" are those recommended by Chemical Abstracts for the silicon analogs of fluorene, xanthene, and thiaxanthene, respectively. See Tables 14 and 15 for cyclic silicon compounds having two or more silicon atoms (each within a cyclic group).

Table 7. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
5-n-Dodecyl-5-phenyldibenzosilole		mb. 330; vol. 440-445; yel. condensate; no res.	Gorsich[c]	8-III
5-(3-Biphenylyl)-5-n-dodecyldibenzosilole		brn. condensate at 400; vol. 430	Gorsich[c]	8-IV
5,5-Di-n-tetradecyldibenzosilole		mb. 390; vol. 430-440, then 450; some dec.	Gorsich[c]	8-IV
5-Benzyldibenzosilole	68.5-69.5	vol. 400-410; no dec.	Gorsich[c]	8-IV
5-Phenyldibenzosilole	42-44	mb. 270; vol. 380-390; no dec.	Gorsich[c]	8-IV
5,5-Diphenyldibenzosilole	146-147	mb. 350; vol. 440-450; sl. p. brn. res.; condensate yel.	Gorsich[c]	8-III, 56a
5,5'-Di-n-dodecyl-5,5'-bis(dibenzosilole)	59-61	mb. 410; vol. 470-480; condensate was p. brown	Gorsich[c]	8-IV
B. Phenoxasilin compounds:[d]				
10,10-Dimethylphenoxasilin	78.5-79.0	b.p. 292-297/atm.	Oita	45

Table 7. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
10,10-Di-n-dodecylphenoxasilin	lq.	mb. 335; vol. 460-470; lq. darkened at 445	Miles	12
10,10-Dibenzylphenoxasilin	melts near room temperature	mb. 400; vol. 440-480; some dec. at top of tube	Miles	12
10,10-Diphenylphenoxasilin	178-179	vol. 420-455; no res.	Oita	8-III, 45
C. Phenothiasilin compounds:[d]				
10,10-Dimethylphenothiasilin-5,5-dioxide	160.5-161.5	vol. 400; no dec.	Oita	8-III, 56b
10,10-Diphenylphenothiasilin-5,5-dioxide	208.5-209.0	vol. 450, some dec.; complete dec. 490	Oita	8-III, 56b
D. Spiro compounds:				
5,5'-Spirobi[dibenzosilole]	245-246	mb. 320; yel. 445; vol. 470-480; no dec.	Gorsich[c]	8-III
10,10-Spirobiphenoxasilin	284-285	vol. 460; no dec.; no res.; rmlt. 284-285; carbon analog is similar	Oita	8-II, 45

Table 8. Compounds prepared in This Laboratory which contain two or more silicon atoms bonded only to carbon[a,b,c].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res., residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., compound volatilizes
dec., decomposes, or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
A. Compounds containing two silicon atoms separated by methylene or similar groups:				
[(Methyldiphenylsilyl)-methyl] triphenylsilane	199-200	vol. 460-470; no dec.	Gorsich[c]	8-I
1,1-Bis(triphenylsilyl)-indene	206	mb. 320; p. yel. 400; brn. 425-450 bl. 465; vol. 470	Miller[b]	8-II, 17
1,2-(Ethylene)bis[tris-(2-ethylhexyl)silane]		mb. 390; vol. 420-430; no dec.	Gorsich[c]	8-II
1,2-(Ethylene)bis[tri-n-decylsilane]	30-32	mb. 360; vol. 440-460; no dec.	Gorsich[c]	8-II

[a,b,c]See footnotes a, b, and c, respectively, of Table 1, page 16.

Table 8. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
1,2-(Ethylene)bis[tri-n-hexadecylsilane]	45.0-48.5	mb. 320; vol. 480-488; no dec.	Gorsich[c]	8-II
1,2-(Ethylene)bis[methyldiphenylsilane]	131-132	vol. 440-450; no dec.; sl. res.	Gorsich[c]	8-IV
1,2-(Ethylene)bis[tribenzylsilane]	136-137	mb. 388; vol. 470-480; condensate was yel., res. or.	Gorsich[c]	8-II
1,2-(1,2-Diphenylethylene)bis[triphenylsilane]	250-252		Meen, Tai, Brook	37
1,3(Trimethylene)bis[triphenylsilane]	150-152		Meen	10
1,5-(Pentamethylene)bis-[triphenylsilane]	145-146	mb. 240; bub. 436; yel. 460; vol. 470-480; or. lq. res.	Gorsich[c]	8-IV
1,10-(Decamethylene)bis-[triphenylsilane]	90.3-91.9	mb. 340; vol. 480-490; lq. dark at 420; bl. res. 440	Miles	12
B. Compounds containing two silicon atoms separated by a phenylene group:				
p-Phenylenebis[trimethylsilane]	95.6-96.0	vol. 232-234; no dec.	Bullock	8-I

Table 8. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
m-Phenylenebis[tri-n-decylsilane]		mb. 395; vol. 430-450; no dec.	Gorsich[c]	8-II
p-Phenylenebis[tri-n-decylsilane]		vol. 438-448; no dec.	Gorsich[c]	8-II
m-Phenylenebis[tri-n-hexadecylsilane]	41.0-42.5	mb. 330; vol. 470; no res.; condensate was yel. 420	Gorsich[c]	8-II
m-Phenylenebis[tribenzylsilane]	155.4-157.3	mb. 350; vol. 505-516; yel. condensate; sl. res.	Gorsich[c]	8-IV
p-Phenylenebis[triphenylsilane]	360		Goodman[b], Oita[b]	
[m-(Trimethylsilyl)-phenyl]tribenzylsilane	69-70	mb. 260; vol. 460-465; no res. 480-540	Miles	12
[p-(Trimethylsilyl)-phenyl] tri-n-hexadecyl-silane	lq., 275-280/0.01	mb. 280; vol. 460-470; lq. darkens sl.	Miles	12
[p-(Trimethylsilyl)-phenyl]triphenylsilane	163.0-164.5	mb. 376; vol. 436; condensate was yel.	Meen	8-II, 10

C. Compounds containing two silicon atoms separated by a biphenylene group:

Table 8. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
3,3'-Biphenylenebis-[trimethylsilane]	lq., 103-104/ 0.005	b.p. 333; no dec.	Lichtenwalter	8-IV, 25
4,4'-Biphenylenebis-[trimethylsilane]	84	mb. 310; vol. 346; no dec.	Bullock	8-I
3,3'-Biphenylenebis-[tri-n-butylsilane]	lq., 211-216/ 0.001	mb. 310; vol. 440-445	Miles	12
4,4'-Biphenylenebis-[tri-n-hexadecylsilane] (slightly impure)	lq., 325-330/ 0.04	mb. 400; vol. 470-480; no res.	Miles	12
3,3'-Biphenylenebis-[tribenzylsilane]	125.5-126.5	mb. 320; bub. 500; vol. 520-530; one of two samples darkened sl.	Miles	12
4,4'-Biphenylenebis-[tribenzylsilane]	145.5-146.5	mb. 270; vol. 510-520; lt. am. condensate at 520; no res.	Miles	12
3,3'-Biphenylenebis-[tris(γ-phenylpropyl)-silane] (impure)	glassy material		Miles	12
4,4'-Biphenylenebis-[triphenylsilane]	285.5-286.0	mb. 350; some colorless condensate at 460; vol. 540-550; sl. dec. on side of tube	Miles	12

Table 8. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
3,3'-Biphenylenebis-[cyclopentamethylene-phenylsilane]	lq., 249-252/ 0.005	vol. 482, sl. dec.	Lichtenwalter[c]	8-IV
4,4'-Biphenylenebis-[cyclopentamethylene-phenylsilane]	165.0-165.5	vol. 480; sl. dec.	Lichtenwalter[c]	8-IV
D. Compounds containing two p-(trimethylsilyl)phenyl groups separated by one or more carbon atoms:				
(Benzylidenedi-p-phenylene)bis[triphenylsilane]	315		Miller[b]	17
Phenylbis[p-(trimethylsilyl)phenyl]methanol	290		Miller[b]	17
4,4'-Bis(trimethylsilyl)-benzophenone			Melvin[b], Bullock	
4,4'-Bis(triphenylsilyl)-benzophenone			Oita	
(1,2-Ethylenedi-p-phenylene)bis[trimethylsilane]	147	mb. 320; vol. 358; no dec.	Bullock	8-II
E. Compounds containing two silicon atoms separated by an (oxydiphenylene) group:				
(Oxydi-o-phenylene)bis-[trimethylsilane]	lq., 117-120/ 0.001	mb. 300; vol. 315-320; no res.	Miles	12

Table 8. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
(Oxydi-p-phenylene)bis-[trimethylsilane]	45.0-45.6	vol. 372; no dec.; a sample distilled in an nitrogen atmosphere did not dec.	Miles, Goodman[b]	8-II, 12
(Oxydi-p-phenylene)bis-[tribenzylsilane]	glassy lq., 320/0.001	mb. 420; vol. 540-550; sl. dec.	Miles	12
(Oxydi-o-phenylene)bis-[triphenylsilane]			Oita	
(Oxydi-p-phenylene)bis-[triphenylsilane]	306-307	mb. 410; vol. 485, then 532; am. res.	Goodman[b]	8-II
F. Compounds containing three silicon atoms:				
Diphenylbis[3(trimethylsilyl)propyl] silane	115-117		Meen	10
Di-n-dodecylbis[p-(trimethylsilyl)phenyl] silane	lq., 265-270/0.0025	mb. 380; vol. 450-463; sl. res.; lq. was sl. yel. 460[c]	Miles	12
Diphenylbis[p-(trimethylsilyl)phenyl] silane	163.5-165.0	mb. 382; vol. 438-446; no res.	Meen	8-II, 10
G. Compounds containing four or five silicon atoms:				

Table 8. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
n-Dodecyltris[m-(trimethylsilyl)phenyl] silane	lq., 205-208/0.001	mb. 280; vol. 440-460; no res. 540	Miles	12
n-Dodecyltris[p-(trimethylsilyl)phenyl] silane	68-75	vol. 390; no dec.	Goodman[b]	8-IV, 28
Phenyltris[m-(trimethylsilyl)phenyl] silane	lq., 205-208/0.1, very viscous	mb. 380; vol. 450-460; some brn. lq. 540[c]	Miles	12
Phenyltris[p-(trimethylsilyl)phenyl] silane	189-191	mb. 368; vol. 470-480; yel. condensate	Goodman[b]	8-II
Tris[p-(trimethylsilyl)-phenyl] silane	159-160	vol. 455; sl. dec.	Goodman[b]	8-IV, 28
Tetrakis[p-(trimethylsilyl)phenyl] silane	355-358	mb. 364; vol. 486-496; yel. condensate	Goodman	8-II, 28

Table 9. Compounds prepared in This Laboratory which contain silicon-hydrogen bonds[a,b,c,d].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res., residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., compound volatilizes
dec., decomposes, or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
A. R_3SiH compounds:				
Triethylsilane	lq., 103.5-104.5/ atm.		Smith[b], Curtice[b]	
Triisopropylsilane	lq., 60-61/3.5		Clark	26
Tri-n-butylsilane	lq., 219-220/atm.		Miles	12
Tri-n-decylsilane	lq., 200-206/ 0.005	Distilled under nitrogen, sl. dec. into an alpha-olefin, b.p. 410-420	Miles	12

[a,b,c]See footnotes a, b, and c, respectively, of Table 1, page 16.

[d]For Si-H compounds having Si-Si bonds, see Table 14. See Table 8 for tris[p-(trimethysilyl)-phenyl]silane.

Table 9. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Tri-n-hexadecylsilane	lq., 300-301/ 0.008	mb. 350; vol. 465-470; sl. dec. at top of tube	Miles	12
Triphenylsilane	44-45	mb. 290; vol. 350	Smith[b], Melvin[b], Curtice[b], etc.	8-I
Triphenyldeuterosilane	44-45		Dunn[b]	57
Tris(p-bromophenyl)-silane	107-108		Goodman[b]	
4,4',4''-(Silylidyne)-tris[N,N-dimethylaniline]	157		Dunn[b]	46
Tri-o-tolylsilane	89-90		Smart	39
Tris[m-(trifluoromethyl)-phenyl]silane	lq., 147-150/ 0.05		Goodman[b]	28
Tri-p-tolylsilane	81-83		Brook	51
Tri-1-naphthylsilane	235-236		Brannen[b]	32
Tri-2-biphenylylsilane	168-169	mb. 280; vol. 470; yel. condensate; r.-brn. res.	Oita	8-II, 50

B. $R_2R'SiH$ compounds:

Table 9. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
(p-Chlorophenyl)diphenylsilane	lq., 161-162/1.0		Dunn[b]	58
(p-Methoxyphenyl)diphenylsilane	lq., 183-184/0.15		Dunn[b]	58
3-(Diphenylsilyl)-N,N-dimethylaniline	lq., 176-177/0.1		Dunn[b]	58
4-(Diphenylsilyl)-N,N-dimethylaniline	lq., 187-189/0.11		Dunn[b]	58
Diphenyl-m-tolylsilane	lq., 155-156/1.2		Dunn[b]	58
[m-(Trifluoromethyl)-phenyl]diphenylsilane	lq., 124-129/1.0		Dunn[b]	
Diphenyl-p-tolylsilane	lq., 147-148/0.2		Dunn[b]	58

Table 10. Some compounds prepared in This Laboratory which contain silicon-halogen bonds[a,b,c,d].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res., residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., compound volatilizes
dec., decomposes, or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
A. R_3Si compounds:				
Chlorotriisopropylsilane	lq., 198/atm.		Clark[b]	26
Tri-n-butylchlorosilane	lq., 134-139/16		Miles, Marshall[b]	12, 15
Chlorotri-n-decylsilane	lq., 240-250/1.0	mb. 260; p. yel. condensate 370; vol. 435-440 with much dec.	Miles	12

[a,b,c]See footnotes a,b, and c, of Table 1, page 16.

[d]Since chlorosilanes have been prepared as intermediates for many reactions, some of these compounds may have been missed in this search. Some disilanes and disiloxanes containing Si-Cl bonds will be found in Tables 14 and 15.

Table 10. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Chlorotri-n-hexadecylsilane	lq., 280-281/0.005		Miles	12
Bromotriphenylsilane	126.5-127.5		Smith[b]	
Chlorotris(o-methoxyphenyl)silane			Melvin[b], Katz, Brannen	
4,4',4"-(Chlorosilylidyne)tris[N,N-dimethylaniline]	212-213		Dunn[b]	46
Chlorotri-o-tolylsilane	115.5-116.0		Katz, Smart, Melvin[b], Brannen[b]	39
Chlorotri-1-naphthylsilane	210-211 (corr.)		Brannen[b], Dunn[b], Ingham	32
Bromotri-1-naphthylsilane			Brannen[b]	
Tri-2-biphenylylchlorosilane	242	yel. lq. on melting;	Oita[b]	8-II, 50
Tri-4-biphenylylchlorosilane			Katz	

B. $R_2R'SiCl$ compounds:

Table 10. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Chloro(p-chlorophenyl)-diphenylsilane	lq., 149-150/0.3		Dunn[b]	58
Chloro(p-methoxyphenyl)-diphenylsilane	lq., 189-192/1.0		Dunn[b]	58
3-(Chlorodiphenylsilyl)-N,N-dimethylaniline	lq., 184-185/0.2		Dunn[b]	58
4-(Chlorodiphenylsilyl)-N,N-dimethylaniline	lq., 227-228/2.5		Dunn[b]	58
Chlorodiphenyl-m-tolyl-silane	lq., 150-151/0.05		Dunn[b]	58
Chloro[m-(trifluoromethyl)-phenyl]diphenylsilane	lq., 116-120/0.3		Dunn[b]	58
Chlorodiphenyl-p-tolyl-silane	lq., 147-148/0.2		Dunn[b]	58
Chloro-1-naphthyldi-phenylsilane	(attempted)		Benedict[b]	
C. Miscellaneous chlorosilanes:				
Chloro(cyclotetramethyl-ene)phenylsilane	lq., 140-145/		Lichtenwalter[c]	

Table 10. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Chloro(cyclopentamethylene)phenylsilane	lq., 77-90/0.09		Lichtenwalter[c]	
Chlorophenyldi-p-tolylsilane	99-100		Wu	59
Dichlorodi-o-tolylsilane	74-75		Smart	39
Benzyltrichlorosilane			Miles	

Table 11. Compounds prepared in This Laboratory which contain silicon-hydroxyl bonds[a,b,c,d].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res., residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., compound volatilizes
dec., decomposes, or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
A. R_3SiOH compounds:				
Tri-n-butylsilanol			Marshall[b], Nobis	15
Tribenzylsilanol	104	mb. 244; yel. 340; vol. 400; complete vol. 548	Marshall[b]	8-II
Triphenylsilanol	151-153	mb. 260; pt. vol. 345-350; lq. present to 510	Smith[b], Goodman[b] Brook, Clark[b] Dunn[b], Melvin[b], Brannen[b]	8-I

[a,b,c]See footnotes a, b, and c, respectively, of Table 1, page 16.

[d]Some compounds containing Si-OH bonds also will be found in Tables 14 and 15.

Table 11. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Tris(p-chlorophenyl)-silanol	121		Miller[b]	29
Tris(o-methoxyphenyl)-silanol			Katz	
Tris p-(dimethylamino)-phenyl silanol	183-184		Plunkett[b], Dunn[b]	46
Tri-o-tolylsilanol			Smart, Benedict[b]	
Tri-m-tolylsilanol			Benedict[b]	
Tri-p-tolylsilanol	98	mb. 240; vol. 375-383	Brannen, Dunn[b] Benedict[b], Oita	8-I, 50
Tri-1-naphthylsilanol	208-209		Brannen[b], Dunn[b] Benedict[b]	
Tri-2-biphenylylsilanol	184-186		Oita	50
Tri-4-biphenylylsilanol	200-201	mb. 280; vol. 340	Dunn[b], Katz	8-I, 60
B. $R_2R'SiOH$ compounds:				
n-Butyldiphenylsilanol			Dunn	
[p-(Dimethylamino)phenyl]-diphenylsilanol	65-66		Dunn	46

Table 11. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Diphenyl-p-tolylsilanol	87-88	mb. 230; vol. 255-265	Benkeser, Dunn[b]	8-I, 16
Di-2-biphenylylphenylsilanol	115-116	yel. lq. on melting; mb. 410; vol. 435; no dec.	Oita	8-II, 50
Cyclopentamethylenephenylsilanol	lq., 90-91/	dec. on heating[c]	Lichtenwalter[c]	
C. $R_2Si(OH)_2$ compounds:				
Diphenylsilanediol (dilithium and disodium salts)			Benedict[b], Melvin	
Bis[p-(dimethylamino)-phenyl]silanediol	173-174		Plunkett[b], Dunn[b]	46
Di-o-tolylsilanediol	135.5-136.5		Smart, Benedict[b]	39
Di-p-tolylsilanediol	115-117° dec.		Benedict[b]	
Di-1-naphthylsilanediol			Benedict	
Di-4-biphenylylsilanediol	200-201		Dunn	60

Table 12. Compounds prepared in This Laboratory which contain silicon-alkoxyl bonds[a,b,c,d].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res., residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., compound volatilizes
dec., decomposes, or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
A. R_3SiOR' compounds (listed according to character of R', then according to character of R):				
Methoxytriphenylsilane	53.4-54.5		Brook	61
Methoxytri-o-tolylsilane	101.5-102.0		Smart	62
Tri-p-biphenylylmethoxysilane	158		Miller[b]	63
Ethoxytriisopropylsilane	lq., 200/atm.		Clark	26
Tri-n-butylethoxysilane			Marshall[b]	

[a,b,c]See footnotes a, b, and c, respectively, of Table 1, page 16.

[d]Since many alkoxyl compounds have been used only as intermediates some compounds may have been missed in this search. See Tables 14 and 15 for other Si-OR compounds.

Table 12. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
(2-Hydroxyethoxy)triphenylsilane	111.0-112.5[e]		Smith[b]	64
(2-Methoxyethoxy)triphenylsilane	67-68[e]	yel. on melting; mb. soon after melting; pt. vol. 360; vol. 360-510; brn. 510°	Smith, Dunn[b], Brannen	64
Ethoxytriphenylsilane	64-66		Smith[b], Clark[b], Dunn[b], Hartzfeld, etc.	
Tris(p-chlorophenyl)-ethoxysilane	128		Miller[b]	29
Ethoxytris(o-methoxyphenyl)silane	102-104	mb. 330; vol. 398; no dec.	Smart, Katz	8-I, 39
4,4',4"-(Ethoxysilylidyne)tris[N,N-dimethylaniline]	125-126		Dunn, Plunkett[b]	46

[e]Reference 8-I reports a thermal screening for "(2-hydroxyethoxy)triphenylsilane, m.p. 68-70", which might be (2-methoxyethoxy)-triphenylsilane.

Table 12. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Ethoxytri-o-tolylsilane	143.5-144.0 144.5-145.0	mb. 190; pt. vol. 270-273; vol. 517-522; lq. lt.-brn.	Smart	8-II, 39
[2-(Dimethylamino)ethoxy] tri-o-tolylsilane	68.5-69.5[f]		Smart	62
Ethoxytri-1-naphthylsilane	186.0-186.5	mb. 270; yel. 460; vol. 488-495	Brannen[b]	8-I, 32
Tri-4-biphenylylethoxysilane			Katz	
Ethoxydiisopropylphenylsilane	lq., 75-77/0.3		Melvin[b]	
Propoxytri-o-tolylsilane	101.0-101.5		Smart	62
Isopropoxytri-o-tolylsilane	106.5-107.5		Smart	62
α-Glyceryloxytriphenylsilane	139-142		Summers[b]	
sec-Butoxytriphenylsilane	120-122		Dunn[b]	64

[f]The hydrochloride melts at 188.5-189.5.

Table 12. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
tert-Butoxytriphenylsilane	104	mb. 240; vol. 360-363; no dec.	Brook, Dunn[b], Miller[b]	8-I, 17
Butoxytri-o-tolylsilane	81.5-82.5		Smart	62
Isobutoxytri-o-tolylsilane	109.5-110.0		Smart	62
sec-Butoxytri-o-tolylsilane	57.5-59.0		Smart	62
Benzyloxytriphenylsilane	84.0-84.5	yel. lq. 395; pt. vol. 395; vol. 450	Smith[b], Hartzfeld	8-II, 64
Benzyloxytri-p-tolylsilane	158.5-159.5		Smart	62
Triphenyl(diphenylmethoxy)silane	83-84	mb. 320; vol. 450; no dec.	Wu, Smith[b]	8-I, 65
Triphenyl(di-p-tolylmethoxy)silane	111-112	mb. 300; yel. 410; vol. 432; no dec.	Wu	8-I, 65
Phenoxytriphenylsilane	103-104	mb. 380; vol. 430-436; no dec.	Smart	8-II
Triphenyl-o-tolyloxysilane	72-74		Dunn, Smith	64
Tri-o-tolyl-o-tolyloxysilane	153-154	mb. 300; vol. 432-436; no dec.	Smart	8-II, 39, 62

B. $R_2Si(OR')_2$ compounds:

Table 12. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Diethoxydiphenylsilane	lq.	mb. 230; vol. 292; no dec.	Miller	8-II
4,4'-(Diethoxysilylene)-bis[N,N-dimethylaniline]	lq., 223-230/ 1.0		Smart, Plunkett[b]	39
Diethoxydi-o-tolylsilane	57.0-58.5		Smart	39
Diethoxydimesitylsilane	63-65	mb. 260; vol. 344; no dec.	Smart	8-II, 39
Diethoxydi-1-naphthyl-silane	100-101	mb. 260; vol. 420; no dec.	Brannen[b]	8-I, 32
C. $RSi(OR')_3$ compounds:				
Benzyltriethoxysilane	lq., 245-248/atm.		Clark[b], Melvin[b]	
Triethoxyphenylsilane			Miller[b], Clark[b]	
4-(Triethoxysilyl)aniline	lq., 148-153/16		Clark[b]	
4-(Triethoxysilyl)-N,N-dimethylaniline			Smart	39
Triethoxy-1-naphthyl-silane	lq., 291-293/ atm.		Brannen[b]	32

Table 13. Compounds prepared in This Laboratory which contain other Group IVB elements in addition to silicon and carbon[a,b,c].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res., residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., compound volatilizes
dec., decomposes, or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
A. Compounds containing silicon and germanium:				
Triethyl(triphenylgermyl)-silane	95-97		Gerow[b]	
Triphenyl(triphenylgermyl)silane	351.5-353.0	mb. 430; yel. 440; bl. 480; vol. 498-500; rmlt. 300-310	Gerow[b]	8-I, 66
Tris(triphenylgermyl) silane	α, 188-189 β, 171-172		Goodman[b]	
Tetrakis[p-(trimethylsilyl)phenyl]germane	351-354		Meen	10

[a,b,c]See footnotes a, b, and c, respectively, of Table 1, page 16.

Table 13. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Triphenyl-1-[3-(triphenylgermyl)propyl]-silane	134-135		Meen	10
Triphenyl-1-[5-(triphenylgermyl)pentyl]-silane	137-138		Goodman[b]	
B. Compounds containing silicon and tin:				
Triphenyl(triphenylstannyl)silane	296-298, 289-291	dec. just above the melting point	Wu,[b] Gist Rosenberg[b]	8-I, 35, 67
Tetrakis[p-(trimethylsilyl)phenyl] tin	343-345		Meen	10
Triphenyl(triphenylstannyloxy)silane	141.5		Rosenberg	
C. Compounds containing silicon and lead:				
Triphenyl(triphenylplumbyl)silane			Wu[b]	
Triphenyl(triphenylplumbyloxy)silane	123-124		Summers[b]	

Table 13. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
D. A compound containing silicon, germanium and tin:				
Tris(triphenylgermyl)-triphenylstannylsilane	340-342, dec.		Goodman[b]	

Table 14. Compounds prepared in This Laboratory which contain silicon to silicon bonds[a,b,c,d].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res., residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., comound volatilizes
dec., decomposes, or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
A. R_3SiSiR_3 compounds:				
Hexaethyldisilane	lq., 87-89/2.5, 248-250/atm.		Smith[b]	
Hexabenzyldisilane	192-193	mb. 380; vol. 460-465; no dec.	Ingham,	8-I
Hexaphenyldisilane	360-362	mb. 480; vol. 503-506; rmlt. 358-361	Dunn[b], Wu[b], Smith[b], Honeycutt[b], Goodman[b]	8-I, 59, 60

[a,b,c]See footnotes a, b, and c, respectively, of Table 1, page 16.

[d]This table includes tri- and tetrasilanes, as well as disilanes.

Table 14. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Hexa-p-tolyldisilane	354-356		Wu[b]	59
Hexa-2-biphenylyldisilane (attempted)			Oita	
Hexa-4-biphenylyldisilane	432-434		Dunn[b]	60
B. $R_xR'_{(6-x)}Si_2$ compounds:				
1,1,2,2-Tetramethyl-1,2-diphenyldisilane	lq., 128-130/1.8; m.p. 34-35		Smith[b]	68
1,1,1-Trimethyl-2,2,2-triphenyldisilane	107-108		Smith[b], Eisch Honeycutt, Wu[b] Lichtenwalter	69
1,1-Dimethyl-1,2,2,2-tetraphenyldisilane	85-86		Smith[b]	68
1,2-Dimethyl-1,1,2,2-tetraphenyldisilane	145-146		Smith[b]	
1,1,1-Triethyl-2,2,2-triphenyldisilane	98-99		Smith[b], Wu[b]	
1,1,1-Tri-n-hexadecyl-2,2,2-triphenyldisilane	lq., 325-326/0.001	mb. 400; vol. 440-450; yel. condensate; lq. brn. res.	Miles	12

Table 14. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Pentaphenyl-p-tolyl-disilane	283-285		Wu[b]	59
1,1-Diphenyl-1,2,2,2-tetra-p-tolyldisilane	240-241		Wu[b]	59
1,2-Diphenyl-1,1,2,2-tetra-p-tolyldisilane	240-241		Wu[b]	59
1,1,1-Triphenyl-2,2,2-tri-p-tolyldisilane	262-264		Wu[b]	59
1,1,2-Triphenyl-1,2,2-tri-p-tolyldisilane	226-227		Wu[b]	59
1,1,1,2-Tetraphenyl-2,2-di-p-tolyldisilane	229-230		Wu[b]	59
1,1,2,2-Tetraphenyl-1,2-di-p-tolyldisilane	252-253		Wu[b]	59
Phenylpenta-p-tolyl-disilane	288-290		Wu[b]	59
C. Compounds in which each of the silicon atoms present is within a cyclic group:				
1,1'-Bis[1-n-dodecyl-silacyclopentane]	lq., 119/ 0.005		Lichtenwalter[c]	

Table 14. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
1,1'-Bis[1-n-dodecylsilacyclohexane]	lq., 209-213/0.06	vol. 435; no dec.	Lichtenwalter[c]	8-IV
1,1'-Bis[1-phenylsilacyclohexane]	lq., 168-169/0.005	vol. 411; no dec.	Lichtenwalter[c]	8-IV
1,1'-Bis[1-chlorosilacyclohexane]	70-73		Lichtenwalter[c]	
D. Tri- and tetrasilanes:				
Octaphenyltrisilane	260-262	mb. 420; vol. 490; yel. condensate	Wu[b]	8-II, 71
Decaphenyltetrasilane	359-362	mb. 410; vol. 440-458; condensate was p. yel. lq.	Wu[b]	8-II
E. Disilanes containing H, Cl, OH and OR groups:[e]				
Pentaphenyldisilane	128-129		Goodman[b]	71
Chloropentaphenyldisilane	154-155		Goodman, Wu[b], Hartzfeld	70, 71

[e]See, however, the last compound of section C of this table.

Table 14. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
1,1-Dichloro-1,2,2,2-tetraphenyldisilane	98-101		Wu[b]	59
1,1,1-Trichloro-2,2,2-triphenyldisilane	143-145		Wu[b]	59
Tetra-2-biphenylyldichlorodisilane	221-222	mb. 380; pt. vol. 420; vol. 440; no dec.	Oita	8-II, 50
Pentaphenyldisilanol	134.0-134.5		Goodman[b]	71
Tetra-o-tolyldisilanediol	158.0-158.5	mb. 215; vol. 254-270	Smart, Marshall[b]	8-II, 39
Ethoxypentaphenyldisilane	210.5-212.0		Goodman[b]	71
Benzyloxypentaphenyldisilane	170.0-171.5		Goodman[b]	71

Table 15. Compounds prepared in This Laboratory which contain silicon-oxygen-silicon linkages[a,b,c].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res., residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., compound volatilizes
dec., decomposes, or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
A. R_6Si_2O compounds:				
Hexa-n-butyldisiloxane	lq.	mb. 290; vol. 325; no dec.	Marshall[b]	8-I
Hexabenzyldisiloxane	203-204	mb. 314; vol. 536-546; sl. r. res. 565	Gorsich[b]	8-II
Hexakis(m-fluorobenzyl)-disiloxane	203-205		Lichtenwalter[c]	

[a,b,c]See footnotes a, b, and c, respectively, of Table 1, page 16.

Table 15. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Hexaphenyldisiloxane	227-229	no change to 510; vol. 515; 3 g. were distilled, b.p. 501-502/740, to give 2.52 g., m.p. 210-221	Dunn, Smith, Eisch, Nobis, Oita, Benedict[b], etc.	8-I
Hexakis(p-chlorophenyl)-disiloxane	210		Miller[b]	29
Hexa-p-tolyldisiloxane	226	mb. 290; vol. 520; yel. lq. 520	Benedict[b]	8-I
Hexa-3-biphenylyldisil-oxane	219.5-220.0	dec. slowly over 500; vol. 560 with dec.		8-IV, 25
B. $R_xR'_{(6-x)}Si_2O$ compounds:				
1,3-Dibenzyl-1,1,3,3-tetramethyldisiloxane	lq.	vol. 205; no dec.	Clark	8-II
1,1,1-Trimethyl-3,3,3-triphenyldisiloxane	49-50	mb. 251; vol. 340; no dec.	Benedict[b]	8-I
1,3-Dimethyl-1,1,3,3-tetrakis(p-chlorophenyl)-disiloxane	68-69		Brook, Miller	17
1,1,1-Trimethyl-3,3,3-tri-o-tolyldisiloxane	91.0-91.5	mb. 270; vol. 367	Benedict[b]	8-I, 42
1,1,1-Trimethyl-3,3,3-tri-m-tolyldisiloxane	lq., 165/1.25		Benedict[b]	42

Table 15. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
1,1,1-Trimethyl-3,3,3-tri-p-tolyldisiloxane	81-85		Benedict[b]	42
1,1,1-Triphenyl-3,3,3-tri-p-tolyldisiloxane	212-213		Benedict[b]	42
1,1,1-Triphenyl-3,3,3-tri-m-tolyldisiloxane	191.0-191.5	mb. 300; vol. 510; no dec.	Benedict[b]	8-I, 42
1,1,1-Triphenyl-3,3,3-tri-p-tolyldisiloxane	164.0-164.5	mb. 300; vol. 515; no dec.	Benedict[b]	8-I, 42, 64
1,1,1-Tri-o-tolyl-3,3,3-tri-p-tolyldisiloxane	197.0-197.5		Benedict[b]	42
1,1,1-Tri-m-tolyl-3,3,3-tri-p-tolyldisiloxane	136-137		Benedict[b]	42
C. Compounds in which each of the silicon atoms is within a cyclic group:				
5,5'-Oxybis[5-n-dodecyldibenzosilole]	74-75	mb. 410; most vol. 480; lt. brn. condensate	Gorsich[c]	8-IV
1,1'-Oxybis[1-phenylsilacyclopentane]	lq., 127-129/0.02	vol. 380-390; no dec.	Lichtenwalter[c]	8-IV
1,1'-Oxybis[1-phenylsilacyclohexane]	lq., 131-135/0.02	vol. 405; sl. dec.	Lichtenwalter[c]	8-IV

Table 15. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
1,1'-Oxybis[1-chlorosilacyclohexane]	lq., 70-75/0.004		Lichtenwalter[c]	
D. Miscellaneous compounds:				
1,1,3,3-Tetraphenyl-1,3-disiloxanediol			Benedict	
Hexa-p-tolyltrisiloxane-1,5-diol			Benedict[b]	
Hexa-p-tolylcyclotrisiloxane			Benedict[b]	

Table 16. Miscellaneous organosilicon compounds prepared in This Laboratory[a,b,c].

Abbreviations used in Tables 1-16

am., amber	lq., liquid	r., red
atm., atmospheric pressure	lt., light	res., residue
bl., black	mb., microbubbles begin	rmlt., residue remelts
brn., brown	or., orange	sl., slight or slightly
bub., vigorous bubbling	p., pale	vol., compound volatilizes
dec., decomposes, or decomposition	pt., partial, or part	yel., yellow

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
A. Methanol derivatives:[d]				
[(Methyldiphenylsilyl)-methyl]diphenylmethanol	89-90	mb. 170; pt. vol. 200; vol. 290-300; trace left to 440; sl. p.-brn. res.	Gorsich[c]	8-IV
[(Dibenzylmethylsilyl)-methyl]diphenylmethanol	105-106	most vol. 290-300; no dec.; the condensate crystallized upon seeding	Gorsich[c]	8-IV

[a,b,c]See footnotes a, b, and c, respectively, of Table 1, page 16.

[d]The methanol derivatives given here are those which did not fit under other subheadings in the previous tables. See Tables 2, 5 and 8 for other methanol compounds.

Table 16. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
B. Acids, esters and salts:				
Triphenylsilanecarboxylic acid	183-184		Brook	61
Methyl triphenylsilane-carboxylate	107-109		Brook	61
Sodium salt or triphenylsilanol			Dunn[b]	
p-(Triphenylsilyl)-phenyl benzoate	168-170	mb. 220; discolored at 310; vol. 400	Melvin[b]	8-I
Acetate of triphenylsilanol	93-94		Melvin[b]	72
Acetate of tri-o-tolylsilanol	121.0-121.5		Brook, Smart	72
Stearate of tri-o-tolylsilanol	39-41	mb. 340; vol. 410; no dec.	Smart	8-II, 72
Ethyl β-(triethylsiloxy)crotonate	lq., 108-110/6.0		Clark[b]	9
C. Mercapto, isocyanate and isothiocyanate compounds:				
Tri-o-tolyl(p-tolylmercapto)silane	112-113		Smart	72

Table 16. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
Triphenylsilyl isocyanate			Melvin[b], Hofferth	73
Triphenylsilyl isothiocyanate			Melvin[b], Hofferth	73
D. $R_3SiNR'_2$ compounds:				
N,N-Dimethyl-1,1,1-triphenylsilylamine	80-81		Melvin[b]	74
N,N-Diethyl-1,1,1-triphenylsilylamine	84-85		Melvin[b]	74
N,N-Di-n-butyl-1,1,1-triphenylsilylamine	60-62		Melvin[b]	74
4,4',4"-[(Di-n-butylamino)-silylidyne]tris[N,N-dimethylaniline]	62-64		Dunn	74
N,N-Di-n-butyl-1,1,1-tri-o-tolylsilylamine	123.5-125.0	mb. 340; vol. 410-423; no dec.	Smart	8-II, 72
E. Miscellaneous nitrogen-containing organosilicon compounds:				
Hexaphenyldisilazane	163-166, 172-173	mb. 280; yel. 450; pt. vol. 495; vol. 500-520	Wu, Miles	8-I, 12

Table 16. (Continued)

Compound[a]	M.p. or b.p.[a]	Thermal screening[a]	Investigators[a]	References[a]
N-Phenyl-1,1,1-triphenyl-N-(diphenylmethyl)-silylamine[e]	194.0-194.5	mb. none; p. yel. 310; bl. 320; vol. 415	Wu	8-I
N', N'-Diphenyl-1,1,1-triphenylsilylhydrazine[f]	140-141	lt.-brn. lq. 190; dark-brn. 200; bl. 220; vol. 355		8-I

[e]It has not been definitely established as yet if the compound is this or an isomer N-[diphenyl(triphenylsilyl)methyl] aniline.

[f]This compound is recorded in Reference 8-I, but was not found in any other source. Mr. L. O. Moore of This Laboratory was unsuccessful in an attempted preparation of this compound.

Bibliography on Organosilicon Compounds Prepared in This Laboratory

The bibliography which follows has been prepared not only for use as reference material to be used in Tables 1-16, but also for the convenience of those doing research on organosilicon chemistry in This Laboratory. The author has attempted to include in the three lists within this bibliography all publications relating to organosilicon chemistry from This Laboratory with the exceptions of References 6 and 8 which have been given previously.

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A Brief Review of the Recent Literature

The following review, as noted previously, is devoted to a summary of recent experimental results closely related to the results reported in this Thesis. The literature was reviewed from 1952 to May, 1957 by using the subject indexes of Chemical Abstracts and by scanning the lists of organometallic and organometalloid publications appearing in the recent issues (January, 1955 - April, 1957) of Current Chemical Papers. The tables of contents of some recent chemical journals also were scanned for related articles. Earlier work of interest was included when it was related to the present study.

Tetraoranosilanes containing long-chained n-alkyl groups.

The author found no articles, other than those from This Laboratory, which reported the preparation of teraorganosilanes containing n-alkyl groups with ten or more carbon atoms in any such group. Petrov and Chernyshev[107] reported the preparation of tetraoctylsilane and a group of other tetraalkylsilanes containing octyl, heptyl and hexyl groups in combination with various shorter alkyl groups. A series of similar medium-length alkyl groups were incorporated into tetraorganosilanes by an investigator from This Laboratory[10]. See Tables 1-4 for these compounds.

It was of interest to the author that a mixture of two tetraalykl silanes (tetraethyl- and tetra-n-propylsilane) containing short-chained

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[107] A. D. Petrov and E. A. Chernyshev, Doklady Akad. Nauk S. S. S. R., 86, 737 (1952); [C. A., 47, 8010 (1953)].

alkyl groups were heated[108] in the presence of aluminum chloride and found to give almost statistical yields of all the possible redistribution products. In addition to the two starting materials, there were obtained triethylpropyl-, diethyldipropyl- and ethyltripropylsilane.

Several tetraorganosilanes containing long-chained n-alkyl groups were prepared in This Laboratory. A group of tetraalkylgermanes[109] containing such groups also were prepared. The tetraorganosilanes included tetra-n-octadecylsilane and related compounds[11], and compounds containing, in addition to the long-chained groups, aralkyl[13, 110, 111], isomeric octyl[10], fluorobenzyl[112], and various other groups. The compounds appear in Tables 1, 2, 3, 4, 7 and 8; the reader is referred to these tables for further information.

Tetraorganosilanes containing aralkyl groups

Recently Eaborn and Parker[113] prepared a series of benzyltrimethylsilanes which were substituted in the aromatic nucleus. These compounds were used to study the kinetics of the base-catalyzed cleavage of the substituted benzyl groups. The kinetics indicated the mechanism to be

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S_N2; electron-withdrawing groups on the aromatic ring were found to facilitate the cleavage. In a later article[114], the same authors reported that the hydroxide ion-catalyzed cleavage of (o-, m- or p-trimethylsilylmethyl)-benzoate ions gave kinetic results compatible with "the Brönstead-Bjerrum theory for reaction between two negative ions."

Cason and Brooks[115] found that the reaction of phenyllithium with trichlorovinylsilane gave triphenyl(β-phenylethyl)silane in addition to the expected triphenylvinylsilane. Chugunov and Petrov[116] prepared tribenzyl-1-naphthylsilane and a novel compound, benzyl-1-napthylphenyl-p-tolylsilane. Maienthal, et al.[117] reported the preparation of dibenzyldiphenylsilane as well as the preparation of a compound which was thought to be tribenzylphenylsilane, m.p. 127-128°. Later they showed, with the help of this investigator[13], that the compound was actually tetrabenzylsilane. The author has successfully prepared tribenzylphenylsilane, m.p. 59-60°[13].

As may be noted from Tables 1, 2, 3, 4, 7 and 8, many tetraorganosilanes containing aralkyl groups (either alone or in combination with other groups) have been prepared in This Laboratory. For further information the reader should consult these tables.

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[117] M. Maienthal, M. Hellman, C. P. Haber, L. A. Hymo, S. Carpenter and A. H. Carr, J. Am. Chem. Soc., 76, 6392 (1954).

Tetraorganosilanes containing fluoro- or chlorophenyl groups

Chvalovský and Bažant[118] reported the preparation of (p-fluorophenyl)-trimethyl- and bis(p-fluorophenyl)dimethylsilane and the use of these compounds to study the nitric acid cleavage of the aryl groups. The products of the reaction were nitroaryl compounds and disiloxanes. This was the only article found giving reference to tetraorganosilanes containing fluorophenyl groups, although several chlorosilanes, disiloxanes, and other compounds containing fluorophenyl groups were listed in a recent review[7b].

The article by Chvalovský and Bažant[118] also reported that the nitric acid cleavage of (p-chlorophenyl)trimethyl- and bis(p-chlorophenyl)-dimethylsilane gave similar results to those obtained with the fluorophenyl compounds. Benkeser and Krysiak[119] prepared (m-chlorophenyl)trimethylsilane from m-chlorophenyllithium and trimethylchlorosilane (the compound previously had been prepared from a Grignard reagent and trimethylchlorosilane[120]). The compound then was cleaved with hydrochloric acid. In later studies[121] (m- and p-chlorophenyl)trimethylsilane were used to prepare the two corresponding (trimethylsilyl)benzoic acids and the acid

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[118] V. Chvalovský and V. Bažant, Collection Czechoslov. Chem. Communs., 16, 580 (1951); Chem. Listy, 46, 158 (1952) [C. A., 47, 8030 (1953)].

[119] R. A. Benkeser and H. R. Krysiak, J. Am. Chem. Soc., 75, 4528 (1953).

[120] J. D. Roberts, E. A. McElhill and R. Armstrong, J. Am. Chem. Soc., 71, 2923 (1949).

[121] R. A. Benkeser and H. R. Krysiak, J. Am. Chem. Soc., 75, 599 (1954).

chlorides. The acid chlorides then were used to prepare ketones by the Friedel-Crafts reaction. Clark, et al.[122] prepared the (o-, m- and p-chlorophenyl)trimethylsilane isomers and used them to prepare the o-, m- and p-biphenylenebis[trimethylsilane] isomers. Patents on several compounds related to those just described were issued to Clark[123, 124]. The electrical moment of (m-chlorophenyl)trimethylsilane was measured by Freiser, et al.[125].

The tetraorganosilanes containing fluorophenyl and chlorophenyl groups which were prepared in This Laboratory are listed in Tables 2-5 and the reader should consult these tables for further information.

Tetraorganosilanes containing (oxydiphenylene) or phenoxyphenyl groups

There have been only a few reported preparations of any silanes containing (oxydiphenylene) or phenoxyphenyl groups. Clark[124] reported the preparation of (oxydi-p-phenylene)bis[dimethylphenylsilane], freezing point -8°. The latter compound is closely related to some compounds reported in this Thesis; the compound was made by coupling two equivalents

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[122] H. A. Clark, A. F. Gordon, C. W. Young and M. J. Hunter, J. Am. Chem. Soc., 73, 3798 (1951).

[123] H. A. Clark (to Dow Corning Corp.), U. S. 2,507,514 and 2,507,515 (May, 1950) [C. A., 45, 2197 (1951)]; (to Dow Corning, Lmtd.), Brit. 669,178 and 669,179 (March, 1952) [C. A., 46, 8894 (1952)].

[124] H. A. Clark (to Dow Corning Corp.), U. S. 2,628,242 (Feb., 1953) [C. A., 47, 9346 (1953)]; (to Dow Corning, Lmtd.), Brit. 671,553 (May, 1952) [C.A., 47, 4909 (1953)].

[125] H. Freiser, M. V. Eagle and J. Speier, J. Am. Chem. Soc., 75, 2821 (1953).

of chlorodimethylphenylsilane with one equivalent of bis(p-bromophenyl) ether, using sodium as the coupling agent.

The compound just described and those described in recent publications from This Laboratory[28,40,44] appear to be the only tetraorganosilanes derived from phenyl ether found in the literature. The compounds made in This Laboratory may be found in Tables 2, 3, 4, 5, 7 and 8.

Tetraorganosilanes containing tolyl groups

The preparation of benzyl-1-naphthylphenyl-p-tolylsilane has already been mentioned[116]. The investigators who prepared this compound also reported the preparation of 1-naphthyltri-p-tolylsilane. Clark, et al.[122] prepared the three isomeric trimethyltolylsilanes and compared the infrared spectra of these compounds. Eaborn and Parker[113] prepared benzyltri-p-tolylsilane in connection with their base-catalyzed cleavage studies. Maienthal, et al.[117] prepared phenyltri-p-tolyl-, diphenyldi-p-tolyl- and triphenyl-p-tolylsilane. These same three compounds also were reported shortly afterwards by investigators in This Laboratory[47]. It was found by Chugunov[126] that p-tolylmagnesium bromide and silicon tetrafluoride afforded a 25 percent yield of tetra-p-silane.

Because of the author's interest in the effect of symmetery on the melting point of related tetraorganosilanes, Table 17 has been prepared to illustrate the effect of the isomeric benzyl, o-tolyl, m-tolyl and p-tolyl

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[126] V. S. Chugunov, Izvest. Akad. Nauk, S. S. S. R., Odtel. Khim. Nauk, 860 (1953) [C. A., 49, 914 (1955)]; [Bull. Acad. Sci., U. S. S. R., Div. Chem. Sci., 761 (1953) English translation].

Table 17. Melting points, in °C, of the isomeric compounds having the general formula $(C_7H_7)_x(C_6H_5)_{(4-x)}Si$

Value of x	C_7H_7 Isomer			
	Benzyl	o-Tolyl	m-Tolyl	p-Tolyl
Zero	232	232	232	232
One	91-92	186-187	150-151	140-141
Two	61-62	174	119-120	121-122
Three	59-60	195-196	128-129	182-183
Four	127-128	145,228, 300,344	155-156	232-233

groups on the melting points of compounds containing these groups. All of the compounds in the table were prepared in This Laboratory[13, 28, 39, 41, 47] although a few of them also were prepared in other Laboratories[117]. In addition to the compounds appearing in Table 17, several other tetraorganosilanes containing tolyl groups were prepared in This Laboratory and information about these compounds, as well as the compounds in Table 17, can be found in Tables 2-5.

The melting point data given in Table 17 show that the benzyl isomer is the lowest melting one in each series of isomers. This is to be expected since the C-Si bond is alphatic in character and therefore more mobile. The C-Si bond in the various tolyl compounds is more rigid and therefore causes the melting points of these isomers to be somewhat higher than those of the benzyl compounds.

From Table 17, it may be noted that the m-tolyl isomer melts lower than the other tolyl isomers when x is ether 2 or 3, and lower than all other tolyl isomers except one of the four stereoisomeric tetra-o-tolyl-silanes when x is 4. When x is 1, the p-tolyl compound, rather suprisingly, is the lowest melting tolyl isomer. It is also suprising that in each series of tolyl isomers, the o-tolyl compound (or in the case where x is 4, one of the four stereoisomeric tetra-o-tolylsilanes) melts higher than the other tolyl compounds.

It appears from Table 18, that the preparation of tetraorganosilanes containing either benzyl or m-tolyl groups should be a promising way to lower the melting points of various organosilicon monomers.

Tetraorganosilanes containing biphenylene and biphenylyl groups

Clark[124] was given a patent on the preparation of p-biphenylenebis-[dimethylphenylsilane]. This is the only example which the author found in the literature of a biphenylenebis[silane] compound, although many phenylenebis[silane] compounds are listed in a recent review[7b].

Petrov and Chernysheva[127] prepared 4-biphenylyltrimethyl- and 4-biphenylyltributylsilane, as well as di-4-biphenylyldimethylsilane. They also prepared several dihydrobiphenylylsilanes. Clark, et al.[122] reported the preparation of the three isomeric biphenylyltrimethylsilanes, and a comparison of the infrared spectra of these compounds.

The preparation of tetra-4-biphenylylsilane was carried out by

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[127]A. D. Petrov and T. I. Chernysheva, Doklady Akad. Nauk S. S. S. R., 84, 515 (1952); 89, 73 (1953) [C. A., 47, 3288 (1953); 48, 3916 (1954)].

Table 18. Melting points, in °C, of the isomeric compounds having the general formula $(C_6H_5C_6H_4)_x(C_6H_5)_{(4-x)}Si$

Value of x	$C_6H_5C_6H_4$ Isomer		
	2-	3-	4-
Zero	232	232	232
One	136-137	128-129	158-159
Two	---	134	169-170
Three	184	amorphous	dimorphic 155 172-174
Four	---	137-138	283

Benkeser, et al.[128] by coupling 4-bromobiphenyl and tri-4-biphenylylsilane using sodium-potassium alloy as the coupling agent. Spialter, et al.[129] reported the preparation of the entire $(4\text{-}C_6H_5C_6H_4)_x(C_6H_5)_{(4-x)}Si$ series of compounds where x is 1, 2, 3, or 4. The analogous 3-biphenylyl series of compounds has been prepared by Gilman and Lichtenwalter[25], while the 2-biphenylyl compounds where x is either 1 or 3 have been prepared by Gilman and Oita[50]. The latter investigators found that because of steric factors tetra-2-biphenylylsilane could not be formed even under

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[128]R. A. Benkeser, H. Landeman and D. J. Foster, J. Am. Chem. Soc., 74, 648 (1952).

[129]L. Spialter, D. C. Priest and C. W. Harris, J. Am. Chem. Soc., 77, 6227 (1955).

some rigorous reaction conditions. Table 18 has been prepared to show the effect of the three isomeric biphenylyl groups on the melting points of related compounds containing these groups.

It is evident from Table 18 that 3-biphenylyl groups tend to give the lower-melting isomer.

In addition to the biphenylene and biphenylyl compounds already mentioned, there were prepared in This Laboratory several other tetraorganosilanes containing such groups; the reader is referred to Tables 2-5, 7 and 8 for further information about these compounds.

Steric hindrance in tetraorganosilanes containing cyclohexyl groups

In 1957 it was reported[3a] that two different procedures for the preparation of cyclohexyltriphenylsilane failed to yield any of this product. The two reactions which failed were that of triphenylsilylpotassium with cyclohexyl bromide and that of chlorotriphenylsilane with cyclohexylmagnesium bromide. The failure of these reactions to give the desired product was ascribed to steric hindrance of the cyclohexyl group. In both cases, other products were formed; the formation of some of these products was explained by the occurence of "reduction" reactions probably through the formation of intermediate "quasi-ring" complexes as illustrated in Figure I.

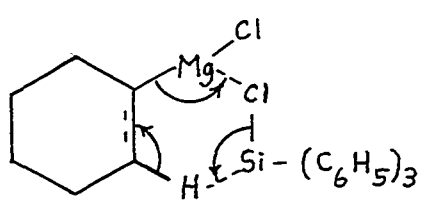

Figure I.
A "quasi-ring" complex

Similar "reduction" processes have been observed in other reactions involving cyclohexyl groups. For example, cyclohexylmagnesium chloride and dicyclohexyl ketone were found to give dicyclohexylmethanol and cyclohexene[130]; the same products also were formed when cyclohexylmagnesium bromide and ethyl cyclohexanecarboxylate were reacted[131]. Cusa and Kipping[132] noted that cyclohexylmagnesium bromide and trichlorophenylsilane yielded a "reduction" product, dicyclohexylphenylsilane.

In 1949, Nebergall and Johnson[133] reported that reaction of silicon tetrachloride and cyclohexyllithium yielded chlorotricyclohexylsilane instead of the expected tetracyclohexylsilane. They not only failed to introduce a fourth cyclohexyl group into the chlorotricyclohexylsilane molecule, but also failed to introduce any other alkyl or an aryl group into the molecule. They were able to replace the chlorine atom by an hydrogen atom by using lithium aluminum hydride and to replace this hydrogen atom by bromine or iodine. The replacement of the bromine by an alkyl group also failed to take place.

However, in 1954, the preparation of two different "tetracyclohexyl

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[130] P. Sabatier and A. Mailhe, Compt. rend., 139, 343 (1904).

[131] A. E. Gray and C. S. Marvel, J. Am. Chem. Soc., 47, 2796 (1925).

[132] N. W. Cusa and F. S. Kipping, J. Chem. Soc., 1040 (1933).

[133] W. H. Nebergall and O. H. Johnson, J. Am. Chem. Soc., 71, 4022 (1949).

silanes" was reported[134, 135]. Two Russian investigators, Petrov and Chernysheva[134], found that cyclohexyllithium and silicon tetrafluoride reacted (when heated in kerosene for a long period) to give a 7.95 percent yield of "tetracyclohexylsilane, m.p. 194°" while reaction of cyclohexyllithium with tricyclohexylfluorosilane yielded the same compound in a yield of 11.3 percent. In Japan, it was found[135] that hydrogenation of tetraphenylsilane, using Raney Nickel as the catalyst, gave "tetracyclohexylsilane, m.p. 279-281°." Both compounds seem to be authentic and it is possible that they are stereoisomers similar to those observed with tetra-o-tolylsilane[41].

The formation of a compound in the germane series which contains a cyclohexyl group was reported recently[136]. This compound was cyclohexyltriphenylgermane, the germanium analog of the compound which Brook and Wolffe[3a] were unable to form by two different procedures described earlier. The germanium compound was made by the addition of triphenylgermane to cyclohexene in the presence of either benzoyl peroxide or ultraviolet irradiation.

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[134] A. D. Petrov and T. I. Chernysheva, Zhur. obschei Khim., 24, 1189 (1954) [C. A., 49, 12276 (1955)]; [English translation in J. Gen. Chem., U. S. S. R., 24, 1179 (1954)].

[135] M. Kanazashi and M. Takakusa, Bull. Chem. Soc. Japan, 27, 441 (1954).

[136] R. Fuchs and H. Gilman, a manuscript (examined by the author of this Thesis) entitled "The Behavior of Triphenylsilane, Triphenylgermane and Triphenyltin Hydride in the Presence of Olefins," has been submitted to the J. Org. Chem. for publication; the article will probably appear late in 1957 or early in 1958.

EXPERIMENTAL

General Procedure

Reagents

Solvents. The ethyl ether employed was either Merck or Mallinckrodt anhydrous ether. The ether was dried and stored over freshly-pressed sodium wire. The tetrahydrofuran employed was dried and distilled over freshly-pressed sodium wire into a flask containing lithium aluminum hydride. When needed, the THF was distilled from the lithium aluminum hydride flask and used immediately. All other solvents used were commercially available "reagent grade" materials. These were dried over sodium when the solvents were to be used in organometallic reactions.

Organic halides. The organic halides used in preparing the various organometallic compounds were generally commercially available "reagent grade" materials. Long-chained n-alkyl bromides employed were obtained from Columbia Chemicals, Inc. Some special halides such as 3,3'-dibromobiphenyl were purchased from Reaction Products, Inc.

Lithium. The lithium wire which was used was the product of the Lithium Corporation of America. The one-eighth inch diameter wire was checked for weight each time a new spool was purchased; the weight was found to vary from 3.0 to 3.7 g. per meter. The wire, purchased with a grease coating, was stored in a dessicator containing "Indicating Drierite". Just prior to use, the desired length of wire was cut from the spool, wiped free of grease and then cut into short pieces, about 4 mm. in length, and allowed to fall into the reaction vessel. During this

operation, a steady stream of dry oxygen-free nitrogen was allowed to flow out of the opening through which the wire was added. After reaction, the excess metal was removed by filtration of the organolithium compound through a loose plug of glass wool.

Magnesium. Commercially available "purified" magnesium turnings were used in all preparations of Grignard reagents. Excess magnesium was removed in the method previously described for excess lithium.

Chlorosilanes. Many of the chlorosilanes employed were purchased materials of "purified" grade. Others were prepared in This Laboratory and these preparations will be described later. The chlorosilanes were usually sealed in glass ampoules until used, although a few compounds were stored in glass-stoppered bottles with a well-greased stopper and then placed inside a dessicator containing "Indicating Drierite".

Silanes. During the present study, several silanes (Si-H containing compounds) were employed. None of these were commercially available. The author prepared some of the compounds used and the preparations are described later. A large amount of triphenylsilane was synthesized by Mr. L. O. Moore of This Laboratory; he kindly supplied the author with enough material for the present study. Mr. E. A. Zuech of This Laboratory prepared tribenzyl- and tris(γ-phenylpropyl)silane in fairly large amounts and allowed the author to use as much as was needed in these studies.

Apparatus

Reaction set-ups. The "usual apparatus" employed in both preparations of the organometallic compounds and the organosilicon compounds consisted

of a standard-taper, 3-necked, round-bottomed flask equipped with an electrically-driven Trubore stirrer, a Friedrichs condenser and, when needed, a dropping funnel. All equipment was dried, prior to use, in an oven held at 110-140°. An inert atmosphere was maintained during the reaction period.

Distillation apparatus. For the distillation of the high-boiling materials produced during this study, a special apparatus was needed. An oven was designed by K. Oita and the author which was well suited as a heat source for such distillations. The oven proper was simply a 5-inch diameter cylinder (closed at the bottom) and approximately 18 inches in height. The lower 5 inches of this was an alundum cylinder with an electrical heating coil wrapped on the outer surface of the cylinder. The central portion of the oven was surrounded by another cylinder 11 inches in diameter. The volume between the inner and outer cylinders was packed with "Dicalite", an insulating material.

The actual distillation was carried out using specially-designed Claisen-type flasks with rotating receivers attached to the side-arms. Because of the high boiling points of the materials made in this study, the most highly reduced pressure possible with the apparatus available was employed. A simple mercury-vapor pump was used in conjunction with an oil-vapor fore-pump and served to give pressures which were generally less than 0.001 mm. of mercury.

Inert atmosphere

Commercially available (99.9 percent pure) nitrogen was further purified by passing it through a train containing a drying tower packed

with "Indicating Drierite", two gas-washing bottles containing one molar vanadyl sulfate[137] and excess lightly-amalgamated, mossy zinc; two gas-washing bottles containing concentrated sulfuric acid; and appropriate traps (i.e., empty gas-washing bottles) in case a back-pressure developed.

Isolation procedure

The products were isolated by a series of steps; the first of which was generally hydrolysis of the reaction mixture (unless a chlorosilane or similar product was being made). Reactions involving Grignard reagents were hydrolyzed with either saturated ammonium chloride solution or with 2 N hydrochloric acid; those involving organolithium reagents were hydrolyzed with water. The "usual work-up" then consisted of the separation of the two phases, extraction of the aqueous phase with ether (usually two 75-100 ml. portions), drying of the combined organic layer and ether extracts over sodium sulfate, filtration to remove the sodium sulfate and distillation of the solvents. The material thus obtained was either distilled or recrystallized with accompanying chromatography, sublimation or other procedures as required.

Physical property determination

Melting points and thermal screenings. Melting points were determined in the normal manner, while thermal screening values, recorded in Tables 1-16, were determined in the previously described manner (see page 12).

Densities, indexes of refraction and molar refractions. The densities of liquids were determined by use of specially-prepared specific gravity

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[137] L. Meites and T. Meites, Anal. Chem., 20, 984 (1948).

bottles of 1-2 ml. capacity. These were calibrated against water at 4° C. The n_D^{20} values were measured on an Abbe refractometer kept at 20°. Calculation of the molar refractions were based on the values of Vogel, et al.[138].

Analyses

The organosilanes, unless containing volatile groups, were analyzed by a reported method[74]. Compounds containing trimethylsilyl groups were analyzed by the Parr Bomb method[139]. The chlorosilanes prepared were analyzed for hydrolyzable chlorine by addition of an amount of the chlorosilane to a mixture of 25 ml. of ethanol (95 percent), 25 ml. of ether and 25 ml. of 0.1 N sodium hydroxide (a slight excess) and then back-titrating the excess sodium hydroxide with 0.1 N sulfuric acid.

Compounds containing bromine were analyzed by a Parr Bomb method[139]. The sodium bromide thus formed was analyzed by a titration method or by precipitation as silver bromide.

Organolithium and Organomagnesium Compounds

During the preparation of the organosilicon compounds frequent use was made of organolithium compounds and organomagnesium compounds. n-Butyllithium and phenyllithium were used in many cases and details of their preparation are not given within the remaining experimental procedure.

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[138]A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, Chem. & Ind. London, 358 (1950); 376 (1951); J. Chem. Soc., 514 (1952); W. T. Cresswell, J. Leicester and A. I. Vogel, Chem. & Ind. London, 19 (1953); J. Phys. Chem., 58, 174 (1954).

[139]Parr Bomb Manual No. 121, Parr Instrument Co., Moline, Illinois (ca. 1949).

The n-butyllithium employed was prepared in essential accordance with the method of Gilman, et al.[140] using, however, a temperature of -40 to -30° during the addition of the n-butyl bromide-ether mixture to the suspension of lithium metal. The phenyllithium used was prepared by the method of Jones and Gilman[141]. The titer of the n-butyllithium was found by the double titration method[142], while that of the phenyllithium was found by a single acid titration method[143]. A few preparations of phenyllithium in tetrahydrofuran (instead of ethyl ether) were made and the details of these are given in the section on cyclohexyltriphenylsilane. The preparative methods for the other organolithium compounds and for the Grignard reagents employed are given in brief form within the procedures for the organosilicon compounds. It should be noted that in the preparation of long-chained n-alkylmagnesium bromides priming of the reaction with a crystal of iodine is often needed to cause the reaction to begin.

Organosilicon Compounds

Tetraalkylsilanes

Tetra-n-dodecylsilane. n-Dodecylmagnesium bromide (1.7 moles, made in 85 percent yield) was prepared from 48.64 g. (2.0 moles) of magnesium

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[140] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, J. Am. Chem. Soc., 71, 1499 (1949).

[141] R. G. Jones and H. Gilman in R. Adams, "Organic Reactions", John Wiley & Sons, Inc., New York, N. Y., 1951, Vol. 6, p. 354.

[142] H. Gilman and A. H. Haubein, J. Am. Chem. Soc., 66, 1515 (1944).

[143] H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, J. Am. Chem. Soc., 45, 150 (1923).

turnings suspended in 100 ml. of ether and a solution of 500.0 g. (2.0 moles) of n-dodecyl bromide in 1000 ml. of ether. The reaction was started by adding a small amount of the alkyl halide solution to the suspension of magnesium turnings. After the reaction commenced the remaining alkyl halide solution was added slowly along with an additional 1000 ml. of ether.

The Grignard reagent was slowly added to 44 g. (0.26 mole) of silicon tetrachloride dissolved in xylene (250 ml.) and then the mixture allowed to stir overnight at reflux. The ether was distilled as completely as possible and was replaced by xylene (no pure material was obtained from a previous run in which the ether was distilled and not replaced by xylene, and in which the residue present after the distillation of ether was heated at 160-180° for four hours). The resulting xylene suspension was refluxed with stirring for 80 hours, cooled and then hydrolyzed by the addition of saturated ammonium chloride. The layers were separated; the water layer was extracted with two large portions of ether; the combined organic layers were dried over sodium sulfate; and the solvents, after filtration of the sodium sulfate, were distilled. The resulting oil was distilled at reduced pressure to yield 150 g. (82 percent) of product, boiling over the range 240-245° (0.06 mm.). This material was redistilled in a Hickman molecular still using a sand-bath temperature of 370° at a pressure of 0.03 mm. This gave 145 g. (79 percent) of product, n_D^{27} 1.4633, d_{27}^{27} 0.8304. These values are identical to those obtained by L. O. Moore[110], who analyzed the product.

Anal. Calcd. for $C_{48}H_{100}Si$: Si, 3.98, MR_D^{138}, 234.7. Found: Si, 4.39,

4.40; MR_D, 234.7.

The infrared spectrum of the product indicated a trace of disiloxane to be present.

Tetra-n-tetradecylsilane. The Grignard reagent, n-tetradecylmagnesium bromide, was prepared in a manner similar to that described for n-dodecylmagnesium bromide. There was obtained from 41.4 g. (0.15 mole) of n-tetradecyl bromide and 3.63 g. (0.15 g.-atom) of magnesium turnings in 250 ml. of ether a yield of 0.133 mole (89 percent) of the Grignard reagent. This was added to 6.0 g. (0.037 mole) of silicon tetrachloride and the mixture allowed to stir at ether reflux. Recalculation indicated that too much silicon tetrachloride had been used. More n-tetradecylmagnesium bromide (0.016 mole) was prepared as before and then added. After refluxing the mixture for 4 hours, the ether was distilled. The residue was heated at 150-160° for 4 hours, then the ether was again added and the mixture was refluxed overnight. After hydrolyzing with dilute hydrochloric acid solution, the mixture was worked up in the usual manner (see page 121) to yield a yellow oil which was distilled at reduced pressure to give 14 g. (47 percent) of material, boiling over the range 225-240° (0.2 mm.). This was redistilled to give 12 g. (40 percent) of an oil, b.p. 253-255° (0.6 mm.), n_D^{27} 1.459, d_{27}^{27} 0.831.

Anal. Calcd. for $C_{56}H_{116}Si$: Si, 3.44; C, 82.26; H, 14.30; MR_D^{138}, 271.89. Found: Si, 3.56, 3.66; C, 81.88, 82.01; H, 14.37, 14.47; MR_D, 269.2.

The infrared spectrum of the product indicated a trace of Si-O-Si

bonding to be present, indicating a small amount of a disiloxane as a possible impurity.

Tetrakis(β-phenylethyl)- and tetrakis(γ-phenylpropyl)silane. Details on the preparation and properties of these compounds have already been published[13]. The reader is referred to this publication for further information.

Cyclohexyltri-n-dodecylsilane (attempted). n-Dodecylmagnesium bromide was prepared in the usual manner from 4.86 g. (0.20 g.-atom) of magnesium turnings and 49.8 g. (0.2 mole) of n-dodecyl bromide using 200 ml. of ether as a solvent. The yield was 0.178 mole (89 percent). This was added in two portions to 12.2 g. (0.056 mole) of trichlorocyclohexylsilane. The first portion (0.112 mole) finally was used up (as indicated by a negative Color Test I[144]) at the end of a reflux period of 20 hours. The remaining Grignard reagent was added, and then most of the ether was distilled and was replaced by dry toluene (100 ml.). The mixture was stirred and refluxed for 48 hours at which time Color Test I was negative. Hydrolysis with saturated ammonium chloride solution and work-up in the usual manner afforded an oil which was distilled at reduced pressure to give several fractions. The major fraction, 13.5 g. (39 percent), was an oily material, n_D^{27} 1.4686, which boiled over the range 235-250° (0.002 mm.).

Anal. Calcd. for $C_{42}H_{86}Si$: Si, 4.54. Found: Si, 5.13, 5.03.

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[144]H. Gilman and F. Schulze, J. Am. Chem. Soc., 47, 2002 (1925).

The infrared spectra of the product from this run and from a previous run both had Si-OH bands present. It appears that some cyclohexyldi-n-dodecylsilanol or similar product must be present thus explaining the high silicon analysis. No further work was done on the separation of this material.

n-Butyltri-n-hexadecylsilane. The preparation of this compound was made from a slightly impure sample of chlorotri-n-hexadecylsilane. n-Butyllithium (0.019 mole), prepared as usual, was added with stirring to 14.0 g. (0.019 mole) of chlorotri-n-hexadecylsilane. After stirring the ethereal solution overnight, Color Test I^{144} was still positive. After stirring for one more hour the mixture was hydrolyzed by the addition of a saturated ammonium chloride solution. Work-up in the usual fashion left ca. 15.0 g. (100 percent) of white solid which could not be crystallized satisfactorily. After distilling the ethanol-ethyl acetate mixture used for the attempted crystallization, the residual material was distilled at reduced pressure to yield 8 g. (53.2 percent) of an oil, boiling over the range 235-255° (0.04 mm.), n_D^{20} 1.4633, d_{27}^{27} 0.834. Redistillation afforded 4.4 g. (29.0 percent) of an oil, boiling at 270-280° (0.001 mm.)

Anal. Calcd. for $C_{52}H_{108}Si$: Si, 3.69; MR_D^{138}, 253.75. Found: Si, 3.63, 3.64; MR_D, 251.58.

An infrared spectrum of the product shows the presence of some disiloxane compound as an impurity.

Benzyltri-n-octadecyl-, tribenzylcyclohexyl-, benzyltri-n-dodecyl- and benzyltris(γ-phenylpropyl)silane. Details on the preparation and

and properties of these compounds have already been published[13]. The reader is referred to this publication for further information.

Dibenzyldi-n-octadecylsilane. Benzylmagnesium chloride (0.068 mole) was prepared in the usual manner (96 percent yield) and then added to 12.1 g. (0.02 mole) of dichlorodi-n-octadecylsilane dissolved in 100 ml. of sodium-dried xylene. The ether was distilled as completely as possible and the reaction mixture then refluxed for 7 hours. The cooled mixture was hydrolyzed with 100 ml. of 3 N hydrochloric acid and then worked-up in the usual manner to yield, after reduced pressure distillation, 7.8 g. (54.5 percent) of an oil, boiling at 317-322° (0.9 mm.), n_D^{20} 1.5005.

Anal. Calcd. for $C_{50}H_{88}Si$: Si, 3.92. Found: Si, 3.92, 4.05.

An infrared spectrum of the product showed the presence of no Si-OH, Si-H or Si-O-Si bands and supported the presence of benzyl and of long-chained n-alkyl groups.

Di-n-octadecylbis(γ-phenylpropyl)silane. Twelve and one-tenth grams (0.02 mole) of dichlorodi-n-octadecylsilane in 50 ml. of sodium-dried xylene was reacted with 0.05 mole of γ-phenylpropylmagnesium bromide in 70 ml. of ether (the Grignard reagent was prepared in the normal way in a yield of 71 percent). The reaction was carried out as in the previous experiment and worked-up in the usual manner (see page 121). Distillation of the crude oil which was obtained, gave 4.8 g. (31 percent) of an oil, boiling at 275-282 (0.001 mm.), n_D^{20} 1.4921, d_4^{20} 0.8872.

Anal. Calcd. for $C_{54}H_{96}Si$: Si, 3.63; MR_D^{138}, 255.0. Found: Si,

3.83, 3.73; MR_D, 254.86.

Trialkylarylsilanes

(m-Bromphenyl)trimethylsilane. m-Dibromobenzene (94 g., 0.40 mole) was reacted with 0.40 mole of n-butyllithium in 600 ml. of ether. The temperature of the mixture was maintained at -35° during the reaction. After stirring for 15 minutes at this temperature, 50.6 ml. (43.2 g., 0.4 mole) of chlorotrimethylsilane was added from a pipet. The mixture was stirred overnight, when Color Test I^{144} was negative. The mixture was hydrolyzed and worked-up in the usual manner (see page 121) to yield, after reduced pressure distillation, 47.8 g. (52.3 percent) of pure material, boiling at 60-65° (0.03 mm.), n^{20}_D 1.5312. Another 19.8 g. (21.3 percent) of crude material was also obtained. The pure material was analyzed.

Anal. Calcd. for $C_9H_{13}BrSi$: Br, 34.89. Found: Br, 34.85, 35.60.

This compound has also been prepared by Benkeser and Krysiak[121] in 17 percent yield, n^{20}_D 1.5290. The m-bromophenyllithium which they used was prepared at room temperature.

Tri-n-butylphenylsilane. To a stirred solution of 0.038 mole of phenyllithium was added 9 ml. (7.0 g., 0.035 mole) of tri-n-butylsilane (preparation given later in this Thesis). A slight amount of cloudiness was noted at this point. The mixture then was refluxed for 6 hours; a gradual appearance of a white precipitate was observed. At this point, Color Test I^{144} was negative and the mixture was hydrolyzed and worked-up as usual. Reduced pressure distillation of the oil obtained was found to

give 3.2 g. (33.2 percent) of phenyltri-n-butylsilane, b.p. 163-166° (10 mm.), n_D^{20} 1.4940, d_4^{20} 0.8757.

Previously reported[15] values for this compound are n_D^{20} 1.4891, d_4^{20} 0.8719.

2-Biphenylyltri-n-decylsilane. A. From chlorotri-n-decylsilane. Chlorotri-n-hexadecylsilane (16.1 g., 0.033 mole) in 100 ml. of ether was stirred with 63 ml. (0.03 mole) of 2-biphenylyllithium in ether for a 3-day period. Color Test I[144] was negative; an additional 21 ml. of 2-biphenylyllithium was added and the mixture stirred over the week-end, and then hydrolyzed and worked-up in the usual manner. Reduced pressure distillation of the crude material afforded 2.5 g. of biphenyl, and 8.9 g. of product, boiling at 260-272° (0.02 mm.). Redistillation of the 8.9 g. fraction yielded 5.0 g. (25.0 percent) of product, b.p. 235-238° (0.001 mm.), n_D^{20} 1.5096, d_4^{20} 0.9087.

Anal. Calcd. for $C_{42}H_{72}Si$: Si, 4.64; MR_D[138], 198.43. Found: Si, 3.66, 4.56; MR_D, 198.02.

An infrared spectrum of the product indicated it to be free of some possible impurities and supported the structure of the desired compound.

B. From tri-n-decylsilane (attempted). To tri-n-decylsilane (14.99 g., 0.033 mole) in 100 ml. of ether was added 63 ml. (0.03 mole) of an ethereal solution of 2-biphenylyllithium (prepared by direct reaction of lithium metal and 2-bromobiphenyl with a yield of 95 percent). After stirring for three days Color Test I[144] was still positive. The

ether was replaced as completely as possible by sodium-dried xylene and another 21 ml. (0.01 mole, total 0.04 mole) of 2-biphenylyllithium was added and the mixture then stirred at reflux for 9 days before Color Test I became weak. Hydrolysis and work-up in the usual way yielded a semi-solid. From this solid was sublimed 5.0 g. of biphenyl, m.p. 65-68°. Distillation of the residue gave no pure material although a small fraction of 0.1 g., boiling over the range 197-210° (0.005 mm.) had an infrared spectrum nearly identical to that of an authentic sample prepared in a different manner although some Si-H compound was present in this fraction.

2-Biphenylyltri-n-butyl- and 2-biphenylyltri-n-hexadecylsilane (attempted). In methods similar to the procedure just described, the reactions of 2-biphenylyllithium with tri-n-butylsilane and with tri-n-hexadecylsilane were found not to yield the desired products.

2-Biphenylyltri-n-dodecylsilane (attempted). Reaction of 2-Biphenylyllithium with chlorotri-n-dodecylsilane (obtained from Anderson Laboratories, Inc.) in a manner similar to the previously described methods yielded 29 percent of material which showed the presence of some Si-OH bands in the infrared spectrum. No further work, except a thermal screening, was done on this material.

2-Biphenylyltri-n-hexadecylsilane. 2-Biphenylyllithium (0.015 mole) in 21 ml. of ether was added to 4.8 g. (0.02 mole) of chlorotri-n-hexadecylsilane and then the mixture was refluxed overnight. Color Test I[144] was still positive; the ether was distilled and replaced by 100 ml.

of toluene. After refluxing for 8 hours, Color Test I was negative. Another 0.015 mole of 2-biphenylyllithium was added and reflux continued (with distillation of the ether) for 48 hours. Color Test I was again negative, so the mixture was hydrolyzed and worked-up in the usual way (see page 121). The biphenyl present in the product was distilled as 5 mm., and the resulting material distilled at reduced pressure to yield 7.0 g. (41 percent) of the desired product, b.p. 283-290° (0.001 mm.), n_D^{20} 1.4840, d_4^{20} 0.870.

Anal. Calcd. for $C_{60}H_{108}Si$: Si, 3.27; MR_D^{138}, 283.40. Found: Si, 3.44, 3.48; MR_D, 282.8.

Infrared spectra of several fractions showed the presence of no Si-H bands. This is in contrast to the results obtained with a sample prepared in a previous run in which somewhat impure chlorotri-n-hexadecylsilane was employed.

Tri-n-dodecylphenylsilane. A. From phenyllithium and chlorotri-n-dodecylsilane. Phenyllithium (0.01 mole) and 5.0 g. (0.0088 mole) of chlorotri-n-dodecylsilane (from Anderson Laboratories, Inc.) were allowed to react. After stirring overnight, Color Test I^{144} was negative. Hydrolysis and work-up in the usual manner yielded, after reduced pressure distillation, 2.6 g. (48.2 percent) of product, b.p. 224-225° (0.001 mm.), n_D^{20} 1.4763.

B. From n-dodecylmagnesium bromide and trichlorophenylsilane. n-Dodecylmagnesium bromide was prepared by the reaction of 40.0 g. (0.16 mole) of n-dodecyl bromide with 4.5 g. (0.185 g.-atom) of magnesium

turnings (160 ml. of ether was used as the solvent). The yield was 99 percent. This was added to 8.5 g. (0.04 mole) of trichlorophenylsilane in 20 ml. of toluene. The ether was distilled and an additional 130 ml. of sodium-dried toluene added. The stirred mixture was refluxed overnight, cooled and then hydrolyzed by the addition of a saturated ammonium chloride solution. Hydrolysis and work-up in the usual manner (see page 121) yielded, after reduced pressure distillation, 12.5 g. (51 percent) of product, b.p. 250-253° (0.001 mm.), n_D^{20} 1.4800, d_4^{20} 0.8595.

Anal. Calcd. for $C_{42}H_{80}Si$: Si, 4.58; MR_D^{138}, 202.89. Found: Si, 4.65, 4.77; MR_D, 201.3.

Tri-n-hexadecylphenylsilane. A. From tri-n-hexadecylsilane. To tri-n-hexadecylsilane (10 g., 0.014 mole) was added 15 ml. (0.02 mole) of 1.33 N phenyllithium solution in two equal portions. Addition of the first 0.01 mole gave complete reaction as judged by a negative Color Test I within 1 hour after addition of the first portion of RLi compound. Color Test I was positive after the second addition, but to insure complete reaction, another 5 ml. (0.0066 mole) of phenyllithium solution was added and the mixture refluxed for 24 hours. Hydrolysis and work-up as usual afforded, after reduced pressure distillation, 3.2 g. (29 percent) of an oil, boiling over the range of 223-230° (0.003 mm.), n_D^{20} 1.4804. Two impure fractions were also collected. The infrared spectrum of the product showed just a trace of Si-H compound to still be present.

B. From trichlorophenylsilane. n-Hexadecylmagnesium bromide was prepared as usual (ca. 0.1 mole) and added to 3.9 g. (0.0187 mole) of trichlorophenylsilane. When Color Test I was negative, the mixture was

hydrolyzed and worked-up in the usual way. Reduced pressure distillation afforded 6.0 g. (42 percent) of product, b.p. 279° (0.2 mm.), n_D^{20} 1.4798, d_{27}^{27} 0.857.

Anal. Calcd. for $C_{54}H_{104}Si$: Si, 3.60; C, 82.99; H, 13.41. Found: Si, 3.66, 3.38; C, 83.11, 83.27; H, 13.39, 13.39.

p-Chlorophenyltri-n-hexadecylsilane. p-Chlorophenyllithium was prepared in the usual fashion from 3.8 g. (0.02 mole) of p-chlorobromobenzene and 20 ml. (0.02 mole) of n-butyllithium at -10 to -20°. To the stirred mixture was added 11.1 g. (0.015 mole) of chlorotri-n-hexadecylsilane (purified material) and stirring was continued until the mixture reached room temperature. Hydrolysis and work-up in the usual way afforded 10.1 g. (82 percent) of product, boiling at 295-300° (0.005 mm.), n_D^{20} 1.4852. Redistillation gave 7.5 g. (61 percent) of an oil, b.p. 250° (0.001 mm.), n_D^{20} 1.4855, d_4^{20} 0.882.

Anal. Calcd. for $C_{54}H_{103}ClSi$: Si, 3.44; MR_D, 266.15. Found: Si, 3.48, 3.49; MR_D, 265.38.

An infrared spectrum supported the structure of the desired compound.

Tri-n-hexadecyl-p-phenoxyphenylsilane. p-Phenoxyphenyllithium (0.045 mole) was prepared from n-butyllithium and p-bromophenyl phenyl ether[145] and then was added to 10 g. (0.035 mole) of chlorotri-n-hexadecylsilane. Color Test I[144] was negative within 15 minutes, and

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[145] W. Langham, R. Q. Brewster and H. Gilman, J. Am. Chem. Soc., 63, 545 (1941).

the mixture was hydrolyzed and worked-up in the usual fashion. There was obtained 6.9 g. (58.5 percent) of an oil, boiling over the range 305-315° (0.005 mm.), n_D^{20} 1.4960, d_{20}^{20} 0.8971.

Anal. Calcd. for $C_{60}H_{108}OSi$: Si, 3.22; MR_D^{138}, 285.18. Found: Si, 3.39, 3.28; MR_D, 284.61.

4-Biphenylyltri-n-hexadecylsilane. 4-Biphenylyllithium (0.025 mole, 85 percent yield) was prepared in the usual way from lithium metal and p-bromobiphenyl and then added to 13.3 g. (0.018 mole) of chlorotri-n-hexadecylsilane. Color Test I^{144} was negative within 15 minutes. Hydrolysis and work-up as usual yielded, after removing biphenyl and quarterphenyl by vacuum sublimation, a semi-solid. This was distilled at reduced pressure to give 6.2 g. (40.2 percent) of a semi-solid product, boiling at 310-323° (0.002 mm.), which was redistilled to give 4.15 g. (27 percent) of product, b.p. 300-310° (0.001 mm.), n_D^{20} 1.5000, d_4^{20} 0.8836.

Anal. Calcd. for $C_{60}H_{108}Si$: Si, 3.27; MR_D^{138}, 283.40. Found: Si, 3.36, 3.56; MR_D, 285.50.

An infrared spectrum confirmed the structure of the desired product.

Tribenzylphenyl-, tris(β-phenylethyl)phenyl- and tris(γ-phenylpropyl)-phenylsilane. The details on these compounds have already been published[13]. The reader should consult this publication for further information.

3-(3'-Bromobiphenylyl)tri-n-butylsilane. To 32.0 g. (0.102 mole) of 3,3'-dibromobiphenyl was added 75 ml. (0.102 mole) of 1.38 N

n-butyllithium in ether. The temperature was kept at -15 to -20° during the addition and for the subsequent reaction time. After stirring at this temperature for 15 minutes, Color Test II[146] was negative. To the stirred organolithium solution was added 23.4 g. (0.100 mole) of tri-n-butylchlorosilane while keeping the temperature at -15 to -20°. After stirring overnight, Color Test I[144] became negative. The reaction mixture was then hydrolyzed and worked-up by the usual procedure. Distillation of the yellow residual oil under reduced pressure afforded 18.2 g. (42 percent) of oil, b.p. 187-191° (0.005 mm.), n_D^{20} 1.5542, d_4^{20} 1.0866.

Anal. Calcd. for $C_{24}H_{35}BrSi$: Br, 18.52; Si, 6.05; MR_D[138], 123.78. Found: Br, analytical results using a Parr Bomb method[139] were erratic and values of 16.4, 16.2, 13.2, and 14.1 were obtained; Si, 6.08, 5.96; MR_D, 127.02.

The compound may possibly be contaminated with either 3,3'-biphenylenebis[tri-n-butylsilane] or 3-biphenylyltri-n-butylsilane.

3-(3'-Bromobiphenylyl)trimethyl- and 3-(3'-bromobiphenylyl)triphenylsilane. Using the above procedure with the appropriate R_3SiCl compound, yields of 60 percent of 3-(3'-bromobiphenylyl)trimethylsilane, boiling at 110-118° (0.001 mm.), n_D^{20} 1.6000; and 12 percent (plus much as yet unpurified material) of 3-(3'-bromobiphenylyl)triphenylsilane, m.p. 95-97°, were obtained. These have not yet been analyzed.

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[146] H. Gilman and J. Swiss, J. Am. Chem. Soc., 62, 1847 (1940).

Dialkyldiarylsilanes

A series of dialkyldiarylsilanes was prepared in which each of the alkyl groups was a long-chained n-alkyl group. These compounds were made by either the reaction of an aryllithium compound with a dialkyldichlorosilane or the reaction of an alkylmagnesium halide with a diaryldichlorosilane. The preparations of each of the Grignard reagents employed in this series of reactions have been described in previous sections. Also, the preparations of some of the aryllithium compounds which were used have been described previously in this Thesis. Exceptions are m-tolyl-, p-tolyl- and 3-biphenylyllithium (each prepared by direct reaction of the corresponding bromo compound with lithium metal); m-fluoro-, m-bromo- and p-(tert-butyl)phenyllithium (each prepared by a halogen-metal interconversion of the corresponding bromo compound with n-butyllithium); and o-phenoxyphenyllithium (the preparation of which is given in the next paragraph). In Table 19, the experimental details for this series of reactions (with the exception of the following example) are given. In Table 20 are summarized the physical properties of the dialkyldiarylsilanes obtained as the major product in the reactions. The following preparation is typical of those found in Table 19.

Di-n-dodecylbis(o-phenoxyphenyl)silane. To 13.6 g. (0.08 mole) of phenyl ether in 100 ml. of ethyl ether was added 63 ml. (0.084 mole) of 1.34 N n-butyllithium. After stirring at room temperature for 24 hours, Color Test II[146] was negative. To the resulting solution was added 17.5 g. (0.04 mole) of dichlorodi-n-dodecylsilane. After refluxing overnight, Color Test I[144] was negative. Hydrolysis and work-up in the usual manner (see page 121) yielded 8 g. (28.8 percent) of product, boiling over the

Table 19. Preparation of some dialkyldiarylsilanes, $R_2SiR'_2$, from RM and R'_2SiCl_2[a]

RM (moles of RM)	R' (moles of R'_2SiCl_2)	Time, hours	Yield, percent	Empirical formula	Analyses, Si, percent Calcd.	Found
m-FC_6H_4Li (0.05)	$C_{12}H_{25}$ (0.023)	<1	71.0	$C_{36}H_{58}F_2Si$	5.04	4.76[b], 4.65[b]
m-ClC_6H_4Li (0.133)	$C_{12}H_{25}$ (0.064)	<1	61.0	$C_{36}H_{58}Cl_2Si$	4.76	4.67, 4.61
p-ClC_6H_4Li (0.133)	$C_{12}H_{25}$ (0.064)	0.33	42.4	$C_{36}H_{58}Cl_2Si$	4.76	4.71, 4.61
p-$PhOC_6H_4Li$ (0.06)	$C_{12}H_{25}$ (0.03)	<1	54.3	$C_{48}H_{68}O_2Si$	3.98	4.00, 3.83
m-MeC_6H_4Li (0.08)	$C_{12}H_{25}$ (0.0355)	<1	67.6	$C_{38}H_{64}Si$	5.12	4.96, 4.91
p-(t-Bu)C_6H_4Li (0.05)	$C_{12}H_{25}$ (0.025)	8	71.5	$C_{44}H_{76}Si$	4.44	4.37, 4.24
2-PhC_6H_4Li (0.081)	$C_{12}H_{25}$ (0.04)	48	48.5	$C_{48}H_{68}Si$	4.17	4.17, 4.14
3-PhC_6H_4Li (0.082)	$C_{12}H_{25}$ (0.04)	8	37.2	$C_{48}H_{68}Si$	4.17	4.15, 4.04
4-PhC_6H_4Li (0.055)	$C_{12}H_{25}$ (0.025)	8	35.6	$C_{48}H_{68}Si$	4.17	3.85, 3.96

[a]The abbreviations "Ph" for phenyl, "Me" for methyl, and "t-Bu" for tert-butyl have been employed.

[b]These Si analyses are slightly low because of the volatilization of some SiF_4 which may form during the oxidation.

Table 19. (Continued)

RM (moles of RM)	R' (moles of R'_2SiCl_2)	Time, hours	Yield, percent	Empirical formula	Analyses, Si, percent Calcd.	Found
$C_{14}H_{29}MgBr$ (0.081)	Ph (0.027)	8[c]	38.0	$C_{40}H_{68}Si$	4.88	4.98, 4.83
$C_{18}H_{37}MgBr$ (0.089)	Ph (0.036)	8[d]	60.0	$C_{48}H_{84}Si$	4.08	3.97, 3.98
p-MeC_6H_4Li (0.1)	$C_{18}H_{37}$ (0.04)	2	68.0	$C_{50}H_{88}Si$	3.92	4.02, 4.03

[c]The ether was distilled and the residue heated dry for 8 hours at 150-160°.

[d]The ether was distilled, and replaced by xylene, the xylene solution was refluxed for 8 hours. This compound has been prepared previously, see Table 3.

Table 20. Physical properties of the dialkyldiarylsilanes, $R_2SiR'_2$, in Table 19.

R[a]	R'[a]	Boiling range, °C(mm.)	n_D^{20}	d_4^{20}	MR_D, Calcd.	MR_D, Found
m-FC_6H_4	$C_{12}H_{25}$	216-220(0.001)	1.4980	----	----	----
m-ClC_6H_4	$C_{12}H_{25}$	260-270(0.008)	1.5110	0.9697	181.46	182.23
p-ClC_6H_4	$C_{12}H_{25}$	275-280(0.005)	1.5160	0.9818	181.46	181.45
p-$PhOC_6H_4$	$C_{12}H_{25}$	275-280(0.001)	1.5380	0.9776	224.10	225.6
m-MeC_6H_4	$C_{12}H_{25}$	245-250(0.001)	1.5101	0.9014	181.04	181.9
p-(t-Bu)C_6H_4	$C_{12}H_{25}$	246-250(0.001)	1.5075	0.9017	209.44	209.14
2-PhC_6H_4	$C_{12}H_{25}$	250-260(0.001)	1.5330	0.9532	220.50	219.25
3-PhC_6H_4	$C_{12}H_{25}$	310-320(0.01)	1.5485	----	----	----
4-PhC_6H_4	$C_{12}H_{25}$	260-272(0.001)	1.5600	0.9803	220.50	221.65
$C_{14}H_{29}$	Ph	252-256(0.2)	1.5013	0.892	189.7	191

[a]See footnote a of Table 19.

Table 20. (Continued)

R[a]	R'[a]	Boiling range, °C(mm.)	n^{20}_D	d^{20}_4	MR_D, Calcd.	MR_D, Found
$C_{18}H_{37}$	Ph	290-292(0.001)[b]	1.5006	----	----	----
p-MeC_6H_4	$C_{18}H_{37}$	308-312(0.002)[c]	1.5210	----	----	----

[b]Di-n-octadecyldiphenylsilane solidified and was found to melt at 33-34°. A sample prepared earlier by this method melted near room temperature. Mr. Mark Hughes, of This Laboratory, has very recently prepared a sample by a different method which melts at 37-38°.

[c]Di-n-octadecyldi-p-tolylsilane solidified and was found to melt near room temperature.

range 260-270° (0.001 mm.), n_D^{20} 1.5290, d_4^{20} 0.9680. Another 7 g. (25.2 percent) of crude product also was obtained.

Anal. Calcd. for $C_{48}H_{68}O_2Si$: Si, 3.98; MR_D^{138}, 224.19. Found: Si, 4.14, 4.12; MR_D, 224.67.

An infrared spectrum supported the structure of the desired compound. Similar spectra were taken and found to be satisfactory for each of the compounds in Tables 19 and 20.

Dibenzyldiphenyl-, diphenylbis(β-phenylethyl)- and diphenylbis(γ-phenylpropyl)silane. In addition to the dialkyldiarylsilanes containing long-chained n-alkyl groups, three diaralkyldiarylsilanes were prepared. These compounds have already been reported[13]. The reader should consult the publication on these compounds (the names of which are given in this paragraph heading) for further information.

Alkyltriarylsilanes

(Methylsulfonylmethyl)triphenylsilane. Dimethylsulfone was prepared by the method of Field and McFarland[147] in 84.5 percent yield. To 9.41 g. (0.1 mole) of dimethylsulfone dissolved in 100 ml. of sodium-dried benzene was added 0.1 mole of n-butyllithium in ethereal solution. The mixture was stirred and refluxed for 3.5 hours at which time 29.4 g. (0.1 mole) of chlorotriphenylsilane was added. After refluxing overnight, Color Test I[144] was negative. After standing several days, the mixture was hydrolyzed by addition of a saturated ammonium chloride solution.

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[147]L. Field and J. W. McFarland, J. Am. Chem. Soc., 75, 5583 (1953).

There was present at the interface between the two liquid phases a large amount of solid material. This was filtered to give 10.5 g. (30 percent) of white solid (melting at 169-174° with some solid remaining). A small amount of dark residue was obtained from evaporation of the ether layer. This residue was added to the 10.5 g. of material. Recrystallization from a petroleum ether (b.p. 77-115°)-benzene (1:1) solvent pair yielded 5.3 g. of product (m.p. 177-178.5°). Another 5.0 g. of slightly impure material (melting at 170-175°) was obtained. The yield of pure material was 14 percent.

Anal. Calcd. for $C_{20}H_{20}O_2SSi$: Si, 7.98. Found: Si, 8.42, 8.49.

An infrared spectrum of the product in CS_2 solution seems to agree with the fact that sulfone groups are present as well as phenyl groups bonded to silicon. It is possible that the sulfone group may have been reduced to a sulfoxide or sulfide group thus accounting for the high analyses but the spectra do not seem to indicate that such was the case.

Cyclohexyltriphenylsilane. A. From trichlorocyclohexylsilane and phenyllithium in ethyl ether. To trichlorocyclohexylsilane (10.7 g., 0.05 mole) was slowly added, with stirring, 125 ml. (0.15 mole) of 1.25 N phenyllithium in ether. After stirring for 2 hours, Color Test I[144] was negative. An additional 55 ml. (0.08 mole) of phenyllithium solution was added and the mixture stirred for an hour. Hydrolysis with 100 ml. of water and work-up in the usual manner yielded 17.1 g. (100 percent) of crude product (melting over the range 128-140°). This crude material was washed thoroughly with methanol (200 ml.) leaving 12.1 g. of white

solid (melting at 138-146°). Multiple recrystallizations from ethanol, acetone and methanol-ethanol solvent pairs finally afforded 4.5 g. (26.3 percent) of product, m.p. 145-146°.

Anal. Calcd. for $C_{24}H_{26}Si$: Si, 8.20. Found: Si, 8.30, 8.26.

In three other similar experiments near quantitative yields of crude product were obtained, but work-up finally left yields of 1 percent (m.p. 148-149°), 7.8 percent (m.p. 144-146°) and 25.6 percent (m.p. 146-148°). The first fraction from recrystallization of each crude product always had a wide melting range (ca. 145-160°), but no pure product having a higher melting point than 148-149° was ever isolated although fractional crystallization of the first crop was always attempted.

Infrared spectra of each of the products are identical.

B. From trichlorocyclohexylsilane and phenyllithium in tetrahydrofuran. In accordance with a recent procedure[148] phenyllithium (0.196 mole, 96 percent) was prepared in specially-dried tetrahydrofuran. To the stirred solution of phenyllithium 7.35 g. (0.0388 mole) of trichlorocyclohexylsilane was added, keeping the flask at -70° by means of an external Dry Ice-acetone bath. The resulting mixture was stirred at -70° overnight, at -30° for 12 hours, at room temperature (25-28°) for 12 hours (Color Test I[144] was still positive) and then refluxed for 12 hours. Color Test

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[148]H. Gilman and B. J. Gaj, a manuscript (examined by the author) entitled "Preparation and Stability of Some Organolithium Compounds in Tetrahydrofuran" has been prepared and submitted for publication in J. Org. Chem.; it should appear in 1958, or earlier.

I was negative and the mixture was hydrolyzed and worked-up as in the previous experiment to yield 6.85 g. (59 percent) of slightly crude product, melting at 140-143°. Evaporation of the methanol washings yielded another 1.9 g. (17 percent) of very crude material, melting over the range 110-130°. Multiple recrystallizations finally afforded 4.5 g. (34.5 percent) of product, m.p. 145-146°. A mixture melting point with the authentic cyclohexyltriphenylsilane from the previous experiment was not depressed.

C. From cyclohexyllithium and chlorotriphenylsilane. Considerable difficulty was experienced in obtaining a good yield of cyclohexyllithium. The preparation of this reagent has been reported[133] with the use of lithium shot, petroleum ether (b.p. 60-70°) and a period of reflux to cause the reaction to take place. The use of lithium wire in place of lithium shot was found to give yields of ca. 28 percent. Carbonation of one such preparation afforded an 8.2 percent yield of cyclohexanecarboxylic acid. One preparation, in which a small amount of preformed n-butyllithium was used to initiate the reaction, gave a yield of 36 percent. In another experiment, purified n-pentane was used in place of petroleum ether (b.p. 60-70°) but no improvement in yield was obtained.

The cyclohexyllithium prepared by the various ways described was used (with the exception of the carbonated run) to prepare cyclohexyltriphenylsilane.

The following experiment represents the best details available from the several experiments carried out.

To 50 ml. of n-pentane (99 percent pure) was added slightly more than

0.7 g. (0.1 g.-atom) of lithium wire (the surface of which was filed to increase surface area). The stirrer was started and 50 drops of a solution containing 5.9 g. (0.05 mole) of cyclohexyl chloride in 50 ml. of n-pentane was added. Refluxing of the mixture caused no evidence of sponantaneous reaction to be noted, so more alkyl halide solution was added. When about one-half of the halide solution had been added, with intermittent refluxing, the reaction commenced and the remaining alkyl halide solution was added slowly. After refluxing overnight, the solution was filtered. The yield was 0.0143 mole (28.3 percent). This was added with stirring to 3.5 g. (0.012 mole) of chlorotriphenylsilane and then stirred for 48 hours after which Color Test I[144] was negative. Hydrolysis and work-up in the usual manner yielded 3.25 g. (79 percent) of crude product, melting at 135-146°. This was combined with material from another run of equal size which also gave 3.25 g. (79 percent) of product. The combined materials were recrystallized to give 1.6 g. (19.5 percent based on 0.024 mole) of product (m.p. 145-147°). Further recrystallization of the product gave 1.0 g., m.p. 146-148°, of white crystals which did not depress the melting point of authentic cyclohexyltriphenylsilane. The infrared spectrum of the product was identical to that of the authentic material.

D. From cyclohexene and triphenylsilane in the presence of benzoyl peroxide (attempted). In a flask were combined 50 ml. of n-heptane, 8.4 g. (0.1 mole) of cyclohexene, 16.5 g. (0.063 mole) of triphenylsilane[149] and 0.3 g. of benzoyl peroxide. The mixture was refluxed at 75° for 72

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[149]Kindly supplied by Mr. L. O. Moore of This Laboratory.

hours. Cooling and work-up of the mixture gave back 16.5 g. (100 percent) of triphenylsilane (crystallized from cold methanol), m.p. 42-44°.

E. From cyclohexene and triphenylsilane in the presence of chloroplatinic acid (attempted). Since a recent article[150] has reported that chloroplatinic acid is an effective catalyst for the addition to olefins, including cyclohexene, of Si-H compounds, the author attempted the following reaction.

Cyclohexene (10.6 g., 0.126 mole), 16.5 g. (0.063 mole) of triphenylsilane and 0.1 ml. of 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol were combined in a flask, and then stirred and refluxed for 96 hours. Attempts to crystallize the oily product failed, and the material was distilled. Some cyclohexene distilled first followed by 12.0 g. (73 percent) of unreacted triphenylsilane, boiling at 130-140° (0.1 mm.), m.p. 42-44°. There also was obtained 1.4 g. of an oily solid, melting over the range 100-175°, and 0.12 g. of a solid, melting over the range 140-170°. Recrystallization of the latter two compounds finally afforded 0.8 g. of a solid (melting at 200-220°) and 0.05 g. of very impure cyclohexyltriphenylsilane (melting at 145-160°). An infrared spectrum of the material melting at 200-220° indicated that some cyclohexyl groups might be present, but also indicated that the compound was mainly hexaphenyldisiloxane. The infrared spectrum of the lower melting material indicated it be crude cyclohexyltriphenylsilane containing some hexaphenyldisiloxane. Triphenylsilanol depressed the melting point of this material, but cyclohexyltriphenylsilane did not.

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[150] J. L. Speier, J. A. Webster and G. H. Barnes, J. Am. Chem. Soc., 79, 974 (1957).

Other experiments on cyclohexyltriphenylsilane. In addition to the previous experiments, the preparation of cyclohexyltriphenylsilane was attempted by two other procedures. Thus, triphenylsilyllithium and cyclohexyl bromide were found to yield a large amount of hexaphenyldisilane as well as liquid fractions which seemed to be mixtures of cyclohexyl bromide and cyclohexene. Since other workers[3a] found similar results using triphenylsilylpotassium, no further work was done on this preparation. The second method attempted was the reaction of cyclohexylmagnesium chloride (in either tetrahydrofuran or ether) with chlorotriphenylsilane. Neither procedure yielded any cyclohexyltriphenylsilane thus confirming the results of earlier workers[3a].

n-Dodecyltri-m-tolylsilane. To 15 g. (0.0495 mole) of trichloro-n-dodecylsilane was added 200 ml. (0.15 mole) of 0.8 N m-tolyllithium in ether (m-tolyllithium prepared in the normal manner from lithium metal and m-bromotoluene). After stirring for 15 minutes, Color Test I[144] was negative and the mixture was hydrolyzed and worked-up as usual. The 20 g. of crude product was fractionated at reduced pressure giving 11.4 g. (49.0 percent) of product, boiling range 196-206° (0.001 mm.), n_D^{20} 1.5488, d_4^{20} 0.9624.

Anal. Calcd. for $C_{33}H_{46}Si$: Si, 5.97; MR_D[138], 154.56. Found: Si, 6.08, 6.07; MR_D, 155.56.

Triphenyl(β-phenylethyl)- and triphenyl(γ-phenylpropyl)silane. These two compounds are reported in a recent publication[13]. The reader should consult this publication for further information.

Phenoxasilin compounds

10,10-Dibenzylphenoxasilin. A four-necked flask was equipped with a reflux condenser, Tru-Bore mechanical stirrer and two dropping funnels. Into one funnel was placed a solution of 28 g. (0.1 mole) of dibenzyldichlorosilane[151] in 300 ml. of ether; into the other was placed a solution of ca. 0.1 mole of (oxydi-o-phenylene)dilithium[45] in 500 ml. of ether. The two reagents then were added slowly to a stirred mixture of 50 ml. of benzene and 100 ml. of ether at a rate to avoid excess of either reagent. The addition required 2 hours. The mixture then was stirred for 72 hours after which time Color Test I[144] was negative. Hydrolysis and work-up in the usual manner (with the exception that not all the benzene was distilled from the product) was followed by chromatography on an alumina column to remove any silanol which might be present. Elution was with 500 ml. of benzene. The benzene was distilled and then the residue was fractionated at reduced pressure to yield 8.5 g. (27 percent) of product, boiling at 188-194° (0.003 mm.), n_D^{20} 1.6305. A second fraction of 7.8 g. (25 percent), b.p. 194-195° (0.003 mm.), n_D^{20} 1.6322 also was obtained. Both fractions had identical infrared spectra which did not indicate any impurities to be present. The fraction boiling at 194-195° was analyzed.

Anal. Calcd. for $C_{26}H_{22}OSi$: Si, 7.44. Found: Si, 7.21, 7.30.

10,10-Di-n-dodecylphenoxasilin. By essentially the same procedure described in the preceding experiment, except using 0.05 mole quantities, 10,10-di-n-dodecylphenoxasilin was prepared from (oxydi-o-phenylene)-

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[151] Kindly supplied by Mr. E. Zuech of This Laboratory.

dilithium[45] and dichlorodi-n-dodecylsilane. The main product, 4.3 g. (16.5 percent) of an oil, boiled at 247-255° (0.009 mm.), n_D^{20} 1.5135, d_4^{20} 0.9359.

Anal. Calcd. for $C_{36}H_{58}OSi$: Si, 5.25; MR_D[138], 171.98. Found: Si, 4.98, 4.90, 4.89; MR_D, 171.93.

Other phenoxasilin compounds. In addition to the two preceding compounds, attempts were made to prepare 10-chloro-10-n-dodecyl- and 10-benzyl-10-chlorophenoxasilin by reactions of benzyltrichloro- and trichloro-n-dodecylsilane with (oxydi-o-phenylene)dilithium. However, despite precautions to avoid contact with moisture, no pure chlorosilanes could be obtained from these two reactions.

Compounds containing two or more silicon atoms bonded only to carbon

1,10-(Decamethylene)bis[triphenylsilane]. 1,10-(Decamethylene)-dilithium was prepared by use of the normal procedure for the preparation of n-butyllithium[140]. Carbonation of this dilithium reagent in several different experiments gave the crude diacid in yields of ca. 20 percent. There also were obtained quite large amounts of neutral polymeric materials of a waxy character which were insoluble.

Several experiments on the preparation of the bis[silane] compound from the dilithium reagent were carried out. A typical preparation follows: 1,10-(decamethylene)dilithium (0.056 mole) was prepared in 56 percent yield. This was added to 33.0 g. (0.112 mole) of chlorotriphenylsilane. After stirring at room temperature for 1 hour, Color Test I[144] was

negative. The mixture was hydrolyzed. A solid was present at the interface of the two solutions. This was separated and discarded (the insoluble material was shown in earlier experiments to be polymeric in nature). The phases were separated and extracted in the usual manner. Distillation of the solvents (after drying over sodium sulfate) left 36.0 g. (97.5 percent) of crude product. Recrystallization of the material was not successful and so two-thirds of the oily substance was distilled at reduced pressure. This gave 17.6 g. (47.5 percent) of material, b.p. 316-319° (0.04 mm.). The remaining undistilled material was chromatographed on alumina using a benzene eluate, and then was combined with the distilled substance. Multiple recrystallizations from petroleum ether (boiling at 77-115°) afforded 5.4 g. (15.5 percent) of product (m.p. 90-91.6°).

Anal. Calcd. for $C_{46}H_{50}Si_2$: Si, 8.52. Found: Si, 8.55, 8.52.

Several other experiments yielded very small amounts of product although high crude yields were obtained.

Tribenzyl[m-(trimethylsilyl)phenyl]silane. m-(Trimethylsilyl)phenyllithium (0.03 mole) was prepared from 6.9 g. (0.03 mole) of (m-bromophenyl)-trimethylsilane and 0.03 mole of n-butyllithium at ca. -35°. This was added to 9.75 g. (0.3 mole) of tribenzylsilane[151]; the resulting mixture was stirred for 24 hours, and then hydrolyzed and worked-up as usual. The residual oil was distilled under reduced pressure and gave 9.65 g. (71.5 percent) of material, b.p. 180-183° (0.001 mm.). The product was recrystallized from ethanol and yielded 3.1 g. (23 percent) of solid, m. p. 68-69.5°.

Anal. Calcd. for $C_{30}H_{34}Si_2$: Si, 12.46. Found: Si, 11.65, 11.85. (This compound was analyzed by a Parr Bomb method[139]).

An infrared spectrum confirmed the structure of the product to be that of the desired compound.

Tri-n-hexadecyl[p-(trimethylsilyl)phenyl]silane. p-(Trimethylsilyl)-phenyllithium was prepared from 0.6 g. (0.086 mole) of lithium wire and 9 g. (0.039 mole) of (p-bromophenyl)trimethylsilane in 50 ml. of ether. The yield was 0.027 mole (69 percent). The organolithium compound was added to 18.1 g. (0.0246 mole) of chlorotri-n-hexadecylsilane (slightly impure material). After stirring overnight, Color Test I was negative. Hydrolysis and work-up in the usual manner followed by reduced pressure distillation afforded 6.5 g. (31 percent) of an oil, boiling at 275-280° (0.01 mm.), n_D^{20} 1.4777, d_4^{20} 0.854.

Anal. Calcd. for $C_{57}H_{112}Si_2$: Si, 6.58; MR_D[138], 282.03. Found: Si, 6.83, 7.65; MR_D, 282.80. (The compound was analyzed by a Parr Bomb method[139]).

Di-n-dodecylbis[p-(trimethylsilyl)phenyl]silane. The preparation of ca. 0.05 mole of p-(trimethylsilyl)phenyllithium was accomplished by stirring together 11.5 g. (0.05 mole) of (p-bromophenyl)trimethylsilane and 0.05 mole of ethereal n-butyllithium solution. Color Test II[146] was negative immediately. After 15 minutes, 10.0 g. (0.05 mole) of dichlorodi-n-dodecylsilane was added to the lithium reagent. The mixture was stirred overnight; Color Test I[144] then was negative. Hydrolysis and work-up as usual yielded 15.0 g. (98 percent) of crude oil. Distillation at reduced pressure gave 5.5 g. (36.6 percent) of an oil, boiling 265-270°

(0.003 mm.), n^{20}_D 1.5080.

Anal. Calcd. for $C_{44}H_{76}Si_3$: Si, 12.67. Found: Si, 12.98, 13.08. (Analyzed by a Parr Bomb method[139]).

Phenyltris[m-(trimethylsilyl)phenyl]silane. (m-Bromophenyl)-trimethylsilane (20.6 g., 0.09 mole) was reacted with 0.09 mole of n-butyllithium at -35°. The m-(trimethylsilyl)phenyllithium thus formed was added to 4.8 ml. (0.03 mole) of trichlorophenylsilane. After stirring for 5 minutes, Color Test I[144] was negative, so the mixture was hydrolyzed and then worked-up as usual. Reduced pressure distillation afforded 8.8 g. (53 percent) of an oil, boiling at 205-208° (0.1 mm.), n^{20}_D 1.5692. An infrared spectrum indicates the product to be the desired compound.

Anal. Calcd. for $C_{33}H_{44}Si_4$: Si, 20.30. Found: Si, 20.12, 20.68. (Analyzed by a Parr Bomb method[139]).

n-Dodecyltris[m-(trimethylsilyl)phenyl]silane. m-(Trimethylsilyl)-phenyllithium (0.07 mole) was prepared as in the previous experiment and allowed to react with 6.9 ml. (0.0232 mole) of trichloro-n-dodecylsilane in the same manner as described for trichlorophenylsilane in the previous experiment. Work-up yielded, after two distillations, 8.0 g. (54.5 percent) of product, boiling at 200-208° (0.001 mm.), n^{20}_D 1.5280. The infrared spectra indicated that the product was the desired compound.

Anal. Calcd. for $C_{39}H_{64}Si_4$: Si, 17.40. Found: Si, 18.1, 16.7. (The compound was analyzed by a Parr Bomb method[139]; this method is occasionally found to give poor results).

3,3'-Biphenylenebis[tri-n-butylsilane]. 3,3'-Biphenylenedilithium was prepared by the reaction of 0.06 mole of n-butyllithium in ether with 0.028 mole of 3,3'-dibromobiphenyl in 100 ml. of ether. When Color Test II[146] was negative, 14.0 g. (0.06 mole) of chlorotri-n-butylsilane was added to the mixture. After stirring overnight at room temperature, Color Test I[144] was negative. Hydrolysis with water and work-up as usual yielded 3.9 g. (26 percent) of pure material, boiling over the range 211-216° (0.001 mm.), n_D^{20} 1.5232, d_4^{20} 0.919. In addition, 5.2 g. (35 percent) of crude material also was obtained.

Anal. Calcd. for $C_{36}H_{62}Si_2$: Si, 10.20; MR_D, 181.8. Found: Si, 10.18, 9.82; MR_D, 183.25.

4,4'-Biphenylenebis[tri-n-hexadecylsilane]. 4,4'-Biphenylenedilithium was prepared by the reaction of 15 g. (0.049 mole) of 4,4'-dibromobiphenyl in benzene solution with 0.10 mole of n-butyllithium in ethereal solution. The mixture was refluxed for 2 hours. When Color Test II[146] became negative, the dilithium compound was treated with 71 g. (0.096 mole) of chlorotri-n-hexadecylsilane (slightly impure material). The resulting mixture was stirred and refluxed gently for 48 hours at which time Color Test I was negative. Hydrolysis was effected with water. A solid was present at the interface of the two solutions. Addition of 200 ml. of benzene caused the solid to dissolve. Work-up in the normal way was followed by reduced pressure distillation to give 18.5 g. (26 percent) of oil, boiling at 325-330° (0.05 mm.), n_D^{20} 1.4667. This was redistilled to give 10.2 g. (14 percent) of material, boiling at 270-280° (0.005 mm.), n_D^{25} 1.4731, d_4^{20} 0.848.

Anal. Calcd. for $C_{108}H_{206}Si_2$: Si, 3.59; MR_D, 513.92. Found: Si, 3.66, 3.67; MR_D, 516.52.

An infrared spectrum of the product indicates some Si-O-Si compound is present within the material. An Si-H band is also present in the spectrum.

3,3'-Biphenylenebis[tribenzylsilane]. 3,3'-Dibromobiphenyl (0.03 mole) dissolved in 100 ml. of dry benzene was allowed to react with 0.07 mole of n-butyllithium in ether. When Color Test II[146] was negative, 18.1 g. (0.06 mole) of tribenzylsilane[151] was added. After stirring for 72 hours, Color Test I[144] was negative. Hydrolysis and work-up as usual left a solid. Crystallization of this solid from a mixture of chloroform and ethanol yielded 12.5 g. (55 percent) of product, m.p. 125.5-126.5°. Another 5.3 g. of crude material, melting at 121-124°, also was obtained.

Anal. Calcd. for $C_{54}H_{50}Si_2$: Si, 7.44. Found: Si, 7.32, 7.32.

Tribenzylsilane, instead of tribenzylchlorosilane, was used in this and several other experiments for several different reasons. The most important one is, of course, that the reactions will occur with tribenzylsilane as well as with tribenzylchlorosilane. A second reason is the relative ease of obtaining tribenzylsilane by reaction of benzylmagnesium chloride with trichlorosilane, while the formation of tribenzylchlorosilane requires a second step (if formed from tribenzylsilane) or an alternate, rather difficult, synthesis. A third reason for the use of the silane rather than the chlorosilane is the greater ease of handling and storing the silane without danger of extensive hydrolysis.

4,4'-Biphenylenebis[tribenzylsilane]. To 0.03 mole of 4,4'-biphenylenedilithium (prepared by reaction of 4,4'-dibromobiphenyl in a benzene-ether mixture) was added 20 g. (0.066 mole) of tribenzylsilane[151]. The mixture was refluxed overnight. Color Test I[144] then was negative so the mixture was hydrolyzed and worked-up as usual. The resulting solid was recrystallized from a petroleum ether (b.p. 60-70°)-ethyl acetate (10:1) mixture to yield 6.1 g. of small prisms, m.p. 144-145°, and 1.6 g. of larger prisms, m.p. 144-145°. Recrystallization of these materials gave 7.5 g. (33 percent) of pure product, m.p. 145.5-146.5°.

Anal. Calcd. for $C_{54}H_{50}Si_2$: Si, 7.44. Found: Si, 7.36, 7.48.

3,3'-Biphenylenebis[tris(γ-phenylpropyl)silane] (attempted). In a manner similar to the procedure described for 3,3'-biphenylenebis-[tribenzylsilane] using tris(γ-phenylpropyl)silane[151] in place of tribenzylsilane, an attempt was made to prepare 3,3'-biphenylenebis[tris-(γ-phenylpropyl)silane]. An oily product was obtained but attempts to distill it were futile, so molecular distillation in a Hickman still was attempted. This gave 3.4 g. of a product for which analysis was marginal. However, an infrared spectrum seemed to confirm the identity of the "compound" as the desired product.

Anal. Calcd. for $C_{66}H_{74}Si_2$: Si, 6.09. Found: Si, 6.32, 6.32, 6.40.

4,4'-Biphenylenebis[triphenylsilane]. 4,4'-Biphenylenedilithium (0.02 mole) was prepared from 4,4'-dibromobiphenyl and n-butyllithium in a benzene-ether mixture. To this dilithium reagent was added 11.8 g. (0.04 mole) of chlorotriphenylsilane; then the reaction mixture was

refluxed for 3 hours and hydrolyzed. A large amount of solid was present at the interface; since this could not be dissolved, it was filtered. Two grams of material (melting above 200°) was obtained. The mother liquors were concentrated to give 6.0 g. (45 percent) of material. Further concentration finally gave a total of 11.9 g. (92.9 percent) of crude product, m.p. 283.5-286°. Recrystallization of 1.16 g. of the crude product from carbon tetrachloride and then petroleum ether (b.p. 60-70°) yielded 0.85 g. (m.p. 285.5-286°) of pure material. An infrared spectrum seemed to indicate that the product was the desired compound.

Anal. Calcd. for $C_{48}H_{38}Si_2$: Si, 8.37. Found: 8.20, 8.24.

(Oxydi-o-phenylene)bis[trimethylsilane]. (Oxydi-o-phenylene)dilithium (0.073 mole) in 140 ml. of ether was prepared by a published procedure[145]. To the stirred organodilithium compound was added 19 ml. (16.2 g., 0.15 mole) of chlorotrimethylsilane. After refluxing overnight, Color Test I[144] was negative. The mixture was hydrolyzed and worked-up as usual to yield 19.2 g. (87 percent) of a crude oil. Distillation of this oil gave 13.7 g. (59.7 percent) of product, boiling at 117-120° (0.001 mm.), n_D^{20} 1.5415, d_4^{20} 1.432.

Anal. Calcd. for $C_{18}H_{26}OSi_2$: Si, 17.86, MR_D[138], 99.92. Found: Si, 17.56, 17.60; MR_D, 100.35. (Analyzed by a Parr Bomb method[139]).

(Oxydi-p-phenylene)bis[trimethylsilane]. (Oxydi-p-phenylene)-dilithium was prepared by the reaction[152] of 23 g. (0.1 mole) of

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[152]H. Gilman, W. Langham and F. W. Moore, J. Am. Chem. Soc., 62, 2333 (1940).

bis(p-bromophenyl) ether in 200 ml. of benzene and 244 ml. of a 1.23 N ethereal solution of n-butyllithium. To the resulting mixture was added slowly 30 g. (0.277 mole) of chlorotrimethylsilane. After two days at reflux temperature, the reaction mixture was hydrolyzed and then worked-up in the usual manner. There was obtained 24.2 g. (77.3 percent) of an oil, boiling at 124-130° (0.02 mm.), n_D^{20} 1.5372, d_4^{20} 0.993.

Anal. Calcd. for $C_{18}H_{26}OSi_2$: Si, 17.86, MR_D[138], 99.92. Found: Si, 17.7, 17.5; MR_D, 98.84. (The silicon analysis was carried out in a Parr Bomb[139].

Following distillation of part of the product under a nitrogen atmosphere at slightly greater than atmospheric pressure, the product obtained was found to solidify into large rhombohedral crystals. These crystals melted at 44.5-46.5° and were used to seed the undistilled material which gave finer crystals, m.p. 44.5-46.5°. Recrystallization of the total amount of material from petroleum ether (b.p. 60-70°) finally gave 6.3 g. (20 percent) of product, m.p. 45.0-45.6°.

J. J. Goodman[2] also prepared this compound by the same method, but found the index of refraction to be n_D^{20} 1.5430, and the density to be d_{20}^{20} 1.0251 giving an MR_D of 96.2 which did not agree with the calculated MR_D of 99.92. The author of this Thesis checked the values of Mr. Goodman carefully and found them to be n_D^{20} 1.5420 and d_4^{20} 1.013. However, these data still give an MR_D value of 97.7 which is still slightly in error from the calculated value.

(Oxydi-p-phenylene)bis[tribenzylsilane]. (Oxydi-p-phenylene)dilithium was prepared as in the previous experiment (0.025 mole run) and allowed to

react with 15 g. (0.05 mole) of tribenzylsilane[151]. After the reaction mixture had stirred for 1 hour, Color Test I[144] was weak and the reaction mixture was hydrolyzed and worked-up in the usual manner to yield 8.0 g. (41.3 percent) of an oil, b.p. 320-322° (0.001 mm.).

Anal. Calcd. for $C_{54}H_{50}OSi_2$: Si, 7.29. Found: Si, 7.40, 7.35.

Silanes, chlorosilanes and a disilane

Tri-n-butylsilane. Trichlorosilane (100 g., 0.738 mole), cooled in a Dry Ice-acetone bath, was reacted with 0.257 mole of n-butylmagnesium bromide in 1800 ml. of ether by addition of the Grignard reagent to the chlorosilane. After stirring for 3 hours, the mixture was hydrolyzed by pouring into a mixture of crushed ice and 100 ml. of hydrochloric acid. Work-up in the usual way, followed by distillation of the crude product through a Widmer column, afforded 110 g. (74 percent) of a colorless liquid, boiling at 215-220, n_D^{20} 1.4380, d_4^{20} 0.7788.

Anal. Calcd. for $C_{12}H_{28}Si$: MR_D[138], 67.88. Found: MR_D, 67.55.

Jenkins and Post[153a] report the preparation (5 percent yield) of tri-n-butylsilane, b.p. 86-87° (2.5 mm.), n_D^{20} 1.4400, d_{25}^{25} 0.9312. Calculation of the MR_D value using the data of Jenkins and Post for the index of refraction and density gave a value of 56.4, which does not agree with the theoretical value of 67.55[138].

Tri-n-decylsilane. n-Decylmagnesium bromide (0.89 mole, 89 percent

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[153a] J. W. Jenkins and H. W. Post, J. Org. Chem., 15, 552 (1950).

yield) was prepared in the normal manner and added, with stirring, to 42 g. (0.28 mole) of trichlorosilane; the latter compound was cooled externally with a Dry Ice-acetone bath to prevent volatilization. Work-up as in the previous experiment yielded two liquid fractions (distillation was not in a Widmer column, but rather in the usual Claisen-type flask): 41.6 g. (30 percent), boiling over the range 200-206° (0.005 mm.), n_D^{20} 1.4580; and 66.2 g. (61 percent), boiling over the range 206-210° (0.005 mm.), n_D^{20} 1.4582. The latter fraction was analyzed.

Anal. Calcd. for $C_{30}H_{64}Si$: Si, 6.20. Found: Si, 6.18.

Tri-n-hexadecylsilane. In a manner similar to the two previous experiments, 0.87 mole of n-hexadecylmagnesium bromide and 0.237 mole of trichlorosilane in 500 ml. of ether were allowed to react. Work-up as in the previous examples yielded 117.8 g. (70.5 percent) of an oil, boiling at 300-305° (0.008 mm.), which solidified to a white waxy material, m.p. 34-36°. An additional 33.0 g. of crude material also was obtained.

Anal. Calcd. for $C_{48}H_{100}Si$: Si, 3.98. Found: Si, 4.08, 4.08.

An impure sample of the same compound was made by the reaction of 18.5 g. (0.025 mole) of chlorotri-n-hexadecylsilane with 0.7 g. (0.0185 mole) of lithium aluminum hydride in 40 ml. of ether. The yield of product was 10.4 g. (58 percent) of white waxy solid, m.p. 33-35°.

Tri-n-butylchlorosilane. A solution of 41.5 g. (0.206 mole) of tri-n-butylsilane in 100 ml. of carbon tetrachloride was allowed to react, using ice-cooling, with 25 g. (0.35 mole) of chlorine gas. After the theoretical amount of chlorine had passed through the solution, the

reaction mixture became yellow. Distillation of the solvent and then distillation of the crude oil, avoiding contact with moisture, yielded 33.5 g. (75 percent) of a colorless oil, boiling at 134-139° (16 mm.). An additional 10.0 g. of crude material also was obtained.

Anal. Calcd. for $C_{12}H_{27}ClSi$: Cl, 15.10. Found: Cl, 14.75, 14.75.

Tri-n-butylchlorosilane has been made by several different methods. Gilman and Marshall[15] made the compound in 51 percent yield by the reaction of ethyl orthosilicate with n-butylmagnesium bromide to form triethylethoxysilane, then acidification to give the disiloxane and finally treatment with ammonium chloride in sulfuric acid to give tri-n-butylchlorosilane. In 1952, both Noller and Post[153b] and Petrov and Chernyshev[107] prepared it by direct reaction of silicon tetrachloride and n-butylmagnesium bromide. The present procedure is of great advantage since it is easy to prepare the tri-n-butylsilane in high yields (the silane need not be purified before chlorination) and the chlorination also gives high yields of the desired product with essentially none of the usual by-product, di-n-butyldichlorosilane.

Chlorotri-n-decylsilane. As in the previous example, chlorine gas (a total of 0.7 mole) was allowed to react with 0.14 mole of tri-n-decylsilane. Originally only 0.2 mole of chlorine was used, but isolation and analysis of the product indicated incomplete reaction, so the additional 0.5 mole of chlorine gas was allowed to react as completely as

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[153b] D. C. Noller and H. W. Post, J. Am. Chem. Soc., 74, 1361 (1952).

possible. Distillation of the solvent and then of the residual oil yielded 35 g. (51.3 percent) of product, boiling over the range 240-250° (1.0 mm.).

Anal. Calcd. for $C_{30}H_{63}ClSi$: Cl, 7.27. Found: Cl, 7.30, 7.35.

Chlorotri-n-hexadecylsilane. A large supply of this compound was needed for various studies and several preparations were made. Difficulty was experienced in obtaining pure material, mainly because of decomposition of the product during distillation. Several preparations from one equivalent of trichloro-n-hexadecylsilane and two equivalents of n-hexadecylmagnesium bromide gave yields of about 45 percent. A typical experiment using this method is given as method A. The best preparation of this material was found to be from tri-n-hexadecylsilane and chlorine gas, given as method B.

A. From trichloro-n-hexadecylsilane. n-Hexadecylmagnesium bromide (0.804 mole) in 400 ml. of ether was added to 130 g. (0.336 mole) of trichloro-n-hexadecylsilane in ether. The mixture was stirred at ether-reflux for 3 days. The ether then was replaced by 400 ml. of xylene and the mixture refluxed overnight. The solution was filtered in a nitrogen pressure filtration apparatus which had been thoroughly dried. The solvents then were distilled to leave an oil. This was distilled at reduced pressure to give three fractions: 25 g., boiling at 100-110° (0.05 mm.); 25 g., boiling at 230-235° (0.1 mm.); and 150-200 g., boiling at 320° (0.1 mm.). Redistillation of the last fraction again gave three fractions: boiling over the range 92-107° (0.05 mm.); boiling over the

range 230-265° (0.05 mm.); and 118 g., boiling at 295-300° (0.05 mm.). Since it appeared that decomposition was taking place during the distillation, 20 g. of the product was redistilled and again three fractions of similar boiling ranges were obtained. The low boiling fraction (Fraction 1) tentatively has been identified as an alpha-olefin, presumably n-hexadecene-1. A summary of the proof of this identification is given in Table 21.

Anal. Calcd. for $C_{48}H_{99}ClSi$: Si, 3.80. Found: Si, 3.79, 3.59.

B. From tri-n-hexadecylsilane. Chlorine gas (0.2 mole) and 0.167 mole of tri-n-hexadecylsilane in 75 ml. of carbon tetrachloride were reacted in a manner similar to that described previously for the preparation of tri-n-butylchlorosilane. The yield of product, after reduced pressure distillation, was ca. 80 percent (only 0.2 of the product was distilled, the remaining material was used as such). The boiling range of the distilled material was 275-280° (0.005 mm.). An infrared spectrum of the product showed no Si-H by-product to be present. Such bands had been observed from the product made by method A.

Anal. Calcd. for $C_{48}H_{99}ClSi$: Cl, 4.82. Found: Cl, 4.81, 5.02.

1,1,1-Tri-n-hexadecyl-2,2,2-triphenyldisilane. Triphenylsilyllithium (ca. 0.05 mole) was prepared by the lithium metal cleavage of 13.3 g. (0.025 mole) of hexaphenyldisilane using tetrahydrofuran as a solvent. The resulting solution was added in two portions to 17.2 g. (0.02 mole) of chlorotri-n-hexadecylsilane. Color Test I^{144} was negative after the first portion was added, but positive after the second addition. After

Table 21. Comparison of n-hexadecene-1 and fraction 1 from the distillation of chlorotri-n-hexadecylsilane

Property	n-Hexadecene-1	Literature[a]	Fraction 1	Redistilled fraction 1
Infrared spectra	nearly identical to fraction 1	----	nearly identical to n-hexadecene-1	----
n_D^{20}	1.4410	1.4419	1.4395	1.4395[b]
b.p., °C	150-160 (15 mm.)	157 (15 mm.)	100-110 (0.05 mm.)	150-153 (13 mm.)
Br_2/CCl_4	decolorizes[c]	----	decolorizes	decolorizes[c]
MnO_4^-/Me_2CO	decolorizes when hot	----	decolorizes when cold	decolorizes when hot

[a]H. T. Waterman, P. Van't Spikjer and H. A. Van Westen, Rec. trav. chim., 48, 1103 (1929).

[b]The refractive index at 25° of fraction 1 from the distillation of the 20 g. of chlorotri-n-hexadecylsilane was 1.4395; an approximation of n_D^{20} is 1.4410.

[c]It requires 42 drops of a 5 percent solution of bromine in carbon tetrachloride to react with 0.5 ml. of each of these compounds as indicated by decolorization ending at this point.

refluxing for 24 hours, Color Test I was weakly positive. The mixture was hydrolyzed and worked-up as usual. The resulting oil was chromatographed on alumina to remove any silanol and then distilled under reduced pressure to yield 15 g. (78 percent) of a colorless oil, boiling at 320-325° (0.001 mm.), n_D^{20} 1.5142, d_4^{20} 0.9081.

Anal. Calcd. for $C_{66}H_{114}Si$: Si, 5.83; MR_D^{138}, 320.04. Found: Si, 5.70, 5.66; MR_D, 320.99.

Infrared spectra

The author has had infrared spectra taken of each of the pure compounds reported in this Thesis, as well as of many impure fractions, etc. for the purpose of substantiating the presence of various functional groups. No listing has been made in the Thesis of the spectral bands present in each of these spectra; however, the original copies of the spectra are filed with the Institute for Atomic Research, Iowa State College, Ames, Iowa and ozalid copies are filed with Dr. Henry Gilman, Department of Chemistry, Iowa State College, Ames, Iowa.

The author wishes to greatfully acknowledge the service of the Institute for Atomic Research in the preparation of the infrared spectra and to especially thank Drs. M. Margoshes, R. Hedges and V. M. Fassel and Messrs. E. M. Layton and R. M. McCord for running the spectra.

DISCUSSION

Preparation of the Compounds

As noted in the Introduction, a major purpose for carrying out this study was to prepare a series of low-melting organosilicon monomers for possible use as thermally-stable, radiation-resistant lubricants or hydraulic fluids. The preparations of these compounds are discussed in the following sections. A second major purpose, the preparation of correlations about structures, melting points and thermal screenings from the data in Tables 1-16, is discussed later.

Intermediates

The preparation of most of the compounds involved the use of the relatively simple reaction illustrated in Equation I (M is either MgCl, MgBr or Li, x is 0, 1, 2 or 3). The major difficulty in the use of this

$$(4-x)\,RM + R'_xSiCl_{(4-x)} \longrightarrow R'_xSiR_{(4-x)} + (4-x)\,MCl \qquad (I)$$

reaction is connected with the procurement or preparation of the reactants. The use of reactive organometallic compounds (such as the organolithium and Grignard reagents, especially the former) requires the immediate reaction and hence the preparation by the author of any such reagents which are employed. Storage of most organolithium compounds for a long period of time is not satisfactory. A similar statement can be made for chlorosilanes which tend to hydrolyze rapidly in the presence of moisture, although such compounds may be stored for relatively long periods in sealed glass ampoules. In the preparation or reaction of either chlorosilanes or reactive organometallic compounds, the exclusion of moisture

is imperative. In addition, oxygen and carbon dioxide must be excluded from the procedures involving reactive organometallic compounds.

Organometallic compounds. Most of the intermediate RM reagents used in this study were not new with the author. The compounds were made in accordance with published procedures or the preparations were patterned after such procedures. An exception to the rule of most compounds not being new can be found in the case of 3-(3'-bromobiphenylyl)lithium which was made by reaction of n-butyllithium (1 equivalent) and 3,3'-dibromobiphenyl (1 equivalent) at -20°. Carbonation of one such run yielded 48.5 percent of 3'bromobiphenylyl-3-carboxylic acid (m.p. 190-191°)[154]. The lithium compound from another run was reacted with tri-n-butylchlorosilane to yield 3-(3'-bromobiphenylyl)tri-n-butylsilane, but further experiments with this product in an effort to prepare 3- 3'-(tri-n-butylsilyl)-biphenylyllithium failed to yield, after carbonation, any significant amount of carboxylic acid. Attempted metalations of o- and m-chlorophenyl phenyl ether with n-butyllithium also failed to occur under the conditions tried, although a successful metalation of p-chlorophenyl phenyl ether has been reported by others[140, 145].

Chlorosilanes. The preparation of chlorosilanes is usually carried out by a process similar to one of those illustrated in Equations II and III, although other methods occasionally are employed.

$$3\ RM + SiCl_4 \longrightarrow R_3SiCl + 3\ MCl \qquad (II)$$

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[154]See H. R. Snyder, C. Weaver and C. D. Marshall, J. Am. Chem. Soc., 71, 289 (1949) for the preparation of this compound by carbonation of 3-(3'-bromobiphenylyl)magnesium bromide.

$$3\ RX + SiCl_4 + 6\ Na \rightarrow R_3SiX + 3\ NaCl + 3\ NaX \quad . \qquad (III)$$

The preparation of chlorotri-n-hexadecylsilane is illustrated (in Equation IV) as a specific example of such a chlorosilane preparation.

$$2\ n\text{-}C_{16}H_{33}MgBr + n\text{-}C_{16}H_{33}SiCl_3 \longrightarrow (n\text{-}C_{16}H_{33})_3SiCl + MgBr_2 + MgCl_2 . \qquad (IV)$$

The product of such preparations is often difficult to separate because moisture must be excluded to avoid hydrolysis and yet complete removal of the magnesium halide salts must be effected. This is usually accomplished by distillation of any ether used as a solvent (thus rending insoluble the magnesium salts which are soluble as etherates), addition of some hydrocarbon solvent and then filtration under a nitrogen atmosphere. This process is quite difficult and an easier method of preparing chlorosilanes is desirable. Such a method has recently been called to the attention of the author[155]. The conversion of SiH compounds to Si-X compounds (X is I, Br or Cl) is well known[156], as is the preparation of R_3SiH compounds by reaction of Grignard reagents with trichlorosilane[157]. The new method essentially combines the two reactions as is illustrated in Equations V and VI.

$$3\ RMgX + HSiX_3 \longrightarrow R_3SiH + 3\ MgCl_2 \qquad (V)$$

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[155] Dr. H. R. Rosenburg, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, private communication to Dr. H. Gilman on the preparation of chlorosilanes, (1956).

[156] See, for instance, Reference 133.

[157] See, for instance, Reference 2.

$$R_3SiH + X_2 \longrightarrow R_3SiX + HCl \quad . \qquad (VI)$$

Employment of this method avoids any difficult filtration since the intermediate R_3SiH compound can be handled in acid solution, extracted with organic solvents and then isolated in the crude state. This crude material then may be chlorinated in carbon tetrachloride solution, the solvent distilled and the product isolated by either simple distillation or fractional crystallization. The author has prepared tri-n-butylchloro-, chlorotri-n-decyl- and chlorotri-n-hexadecylsilane by this method with very satisfactory results.

Silanes. In many cases the R_3SiH compounds referred to in the previous section need not be converted to the chlorosilane before proceeding with a particular reaction. This is true because the process depicted in Equation VII occurs quite readily with many silanes and organolithium compounds[158] (see, however, the discussion of 2-biphenylyl compounds which follows shortly). There are several reasons why

$$R'Li + R_3SiH \longrightarrow R'SiR_3 + LiH \quad . \qquad (VII)$$

Reaction VII might be preferable in many cases to the corresponding reaction of a chlorosilane. This is, of course, provided that Reaction VII readily occurs with a particular silane and organolithium compound. Among these reasons are the easy formation of many trialkylsilanes from trichlorosilane and Grignard reagents, and the greater ease of handling and storing the silanes thus obtained without danger of hydrolysis.

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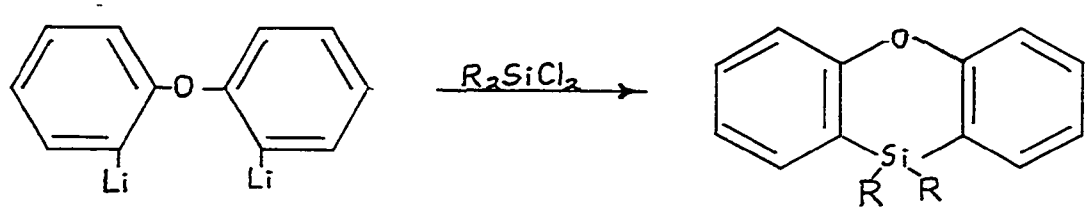
[158] See References 19 and 30, and R. N. Meals, J. Am. Chem. Soc., 68, 1880 (1946).

However, many chlorosilanes are commercially available and it is probably not worthwhile to reduce these compounds to the silanes since the chlorosilane is more reactive towards organolithium compounds than the corresponding silane (see the section on 2-biphenylyl compounds).

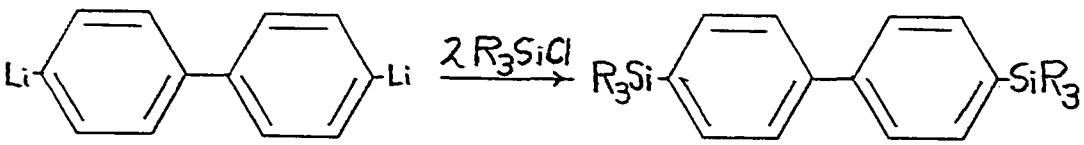
During the course of this work three different silanes were prepared by the reactions of trichlorosilane (silicochloroform) with 3 equivalents each of n-butyl-, n-decyl- and n-hexadecylmagnesium bromides. The product of the latter reaction, tri-n-hexadecylsilane, also was made from chlorotri-n-hexadecylsilane and lithium aluminum hydride.

Compounds for testing

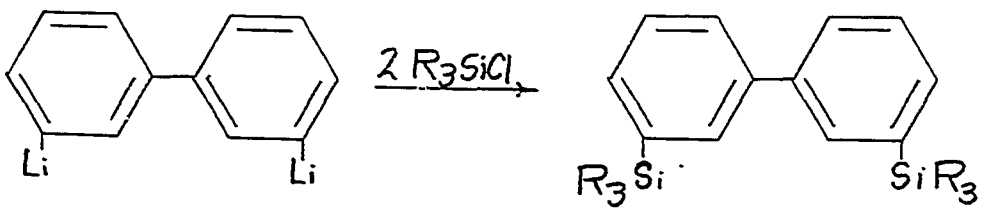
The preparations of the compounds to be used for thermal screening tests and which were to have low-melting points suitable for use as lubricants or hydraulic fluids have been carried out by the methods given in the previous sections of the Discussion. Of special interest are the preparations of the cyclic phenoxasilin compounds (illustrated in Equation IX), the biphenylenebis[silane] compounds (illustrated in Equations X and XI), and the (oxydiphenylene)bis[silane] compounds (illustrated in Equations XII and XIII). These preparations are essentially modifications of either Reaction I or Reaction VII.



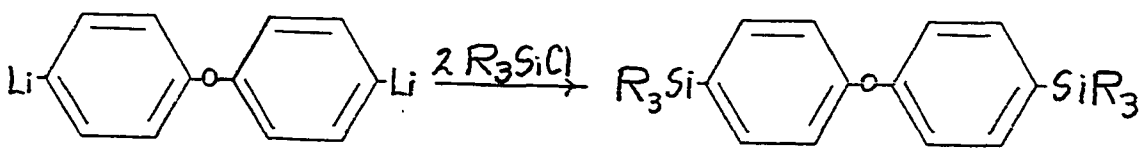
(IX)



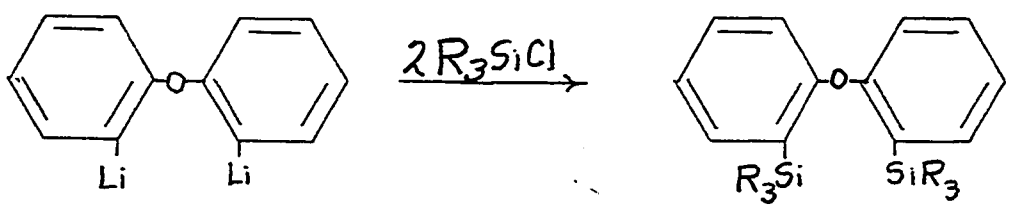
(X)



(XI)



(XII)



(XIII)

2-Biphenylyl compounds. An interesting phase of the preparative work was the differences noted in the reactivity of R_3SiCl compounds and the corresponding R_3SiH compounds towards 2-biphenylyllithium. It was found that three different silanes (tri-n-butyl-, tri-n-decyl- and tri-n-hexadecylsilane) did not react with this organolithium compound although some forcing conditions (72 hours refluxing in xylene solution, for instance) were employed. However, three different chlorosilanes

(chlorotri-n-decyl-, chlorotri-n-dodecyl- and chlorotri-n-hexadecylsilane) did react with 2-biphenylyllithium, although relatively high-boiling solvents at reflux or long reaction times at ether reflux were needed to cause the reaction to proceed. Yields were from 25-40 percent. Another chemist[159] in This Laboratory has noted that reaction of 2-biphenylyllithium with chlorotrimethylsilane (at room temperature during a 24-hour period) gives a 94 percent yield of 2-biphenylyltrimethylsilane; while an identical reaction, using chlorotriethylsilane in place of chlorotrimethylsilane, gives only a 30 percent yield of 2-biphenylyltriethylsilane.

The very high yield of the 2-biphenylyltrimethylsilane when compared to the 30 percent of the triethyl compound obtained under the same conditions and the 25-40 percent yields of the tri-n-decyl, tri-n-dodecyl and tri-n-hexadecyl compounds obtained under somewhat more stringent conditions, seem to indicate that steric hindrance of the 2-biphenylyl group is the most important influence on the yield. Such steric hindrance has been noted previously[50]. Another fact that points to the contribution of steric hindrance is the relatively easy reaction of phenyllithium with tri-n-hexadecylsilane (24 hours at ether reflux) which gives a fair yield (29 percent) of tri-n-hexadecylphenylsilane while reaction of 2-biphenylyllithium with tri-n-hexadecylsilane (several days in refluxing xylene) failed to give any product.

Cyclohexyltriphenylsilane. As noted in the Introduction and Historical, the preparation of cyclohexyltriphenylsilane by two different

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[159]M. B. Hughes, private communication, Iowa State College (1957).

methods failed to give the desired product, apparently because of the steric hindrance associated with the cyclohexyl group. It has been now found that fairly good yields (25-35 percent) of pure cyclohexyltriphenylsilane can be obtained by two different methods (Equations XIV and XV).

$$C_6H_{11}Li + (C_6H_5)_3SiCl \longrightarrow C_6H_{11}Si(C_6H_5)_3 + LiCl \qquad (XIV)$$

$$3\ C_6H_5Li + C_6H_{11}SiCl_3 \longrightarrow C_6H_{11}Si(C_6H_5)_3 + 3\ LiCl\ . \qquad (XV)$$

In the experiments of Brook and Wolffe[3a], it was found that triphenylsilylpotassium and cyclohexyl bromide underwent a halogen metal-interconversion giving rise to bromotriphenylsilane and cyclohexylpotassium. Thus, there was present in their mixture two metallic compounds, triphenylsilylpotassium and cyclohexylpotassium. If the latter compound were present alone, it could undergo a reaction with bromotriphenylsilane similar to that shown in Equation XIV for the corresponding lithium and chloro compounds. The fact that hexaphenyldisiloxane and no cyclohexyltriphenylsilane was found in their reaction seems to indicate that triphenylsilylpotassium is more reactive towards bromotriphenylsilane than cyclohexylpotassium since these metallic reagents were in competition with each other.

Brook and Wolffe[3a], as well as this author, found that no cyclohexyltriphenylsilane was formed when cyclohexylmagnesium bromide (or chloride) was reacted with chlorotriphenylsilane. Since Reaction XIV occurs readily, it appears that the organolithium compound is more reactive than the corresponding Grignard reagent (as expected) towards

displacement of the chloride ion from chlorotriphenylsilane. This is somewhat similar to the increased reactivity of silicon tetrafluoride over silicon tetrachloride towards cyclohexyllithium as noted by Petrov and Chernysheva[134] in the preparation of tetracyclohexylsilane.

Since tetrahydrofuran (THF) is known to increase the reactivity of organometallic compounds in many reactions, attempts were made to use THF as a solvent for cyclohexylmagnesium chloride and for phenyllithium in reactions aimed at the preparation of cyclohexyltriphenylsilane. However, no effect was noted on the reactivity in either case.

Correlations Between Structure and the Target Physical Properties

It has been previously mentioned that one of the major purposes for carrying out this study was to enable the preparation of some correlations. These were to deal with the effect of various groups which have been incorporated into organosilicon monomers on some target physical properties of the monomers. The two major properties with which the author has been concerned are thermal stability and a low-melting point. The compilation of the data in Tables 1-16 was undertaken mainly to aid in the preparation of the correlations, although a secondary purpose of the compilation was to make a survey of the past work on organosilicon compounds carried out in This Laboratory.

The author recognizes that absolute correlations about the effect of structure on physical properties are not absolute and are, of necessity, empirical in nature. Nevertheless such data are helpful in

indicating future lines of research and in pointing out the most favorable, or least favorable, groups with which to work. A complete correlation of every compound in Tables 1-16 against one another and the target properties is an undertaking beyond the scope of a Thesis such as this. Therefore, the correlations which follow have been limited mainly to the work of the author, although data on other compounds from the tables have been used freely. Further correlations on other compounds easily may be made by those interested in such information.

Melting point relationships

The following discussion has been divided into several sections to aid in making comparisions. Instead of discussing the various dissymmetrical groups as a unit, sections have been devoted to the tolyl groups, biphenylyl groups, and so forth.

Compounds containing long-chained n-alkyl groups. An earlier worker[2] from This Laboratory has observed that long-chained n-alkyl groups tend to give low-melting organosilicon compounds when such groups are combined into tetraorganosilanes. This observation is supported in part by the data in Tables 1 and 4. The melting points of the alkyltriphenylsilanes given in Table 4 are very interesting. Methyltriphenylsilane melts at 66-67°. Starting at 66-67°, the melting point then increases as the length of the chain increases in ethyl-, propyl- and butyl- triphenylsilane. As the chain of the alkyl group lengthens in hexyl-, octyl-, and n-decyltriphenylsilane, the melting point decreases and then lies on an approximate plateau as the chain length increases in dodecyl-, tetradecyl-, hexadecyl-, heptadecyl- and octadecyltriphenylsilane. However, there is a

slight monotonic increase in melting point as the chain lengthens from 16 to 18 carbon atoms.

The data in Table 1 illustrate the fact that most of the symmetrical R_4Si compounds with long-chained groups are liquids thus proving that such groups tend to give low-melting tetraorganosilanes. However, it should be noted that the melting point apparently increases with increase in chain length since all the tetraalkylsilanes with long-chained n-alkyl groups melt below room temperature with the exception of tetra-n-hexadecylsilane, m.p. 38.5-40.0°, and tetra-n-octadecylsilane, m.p. 50.0-50.5°. A similar effect is noted in the dialkyldiphenylsilanes which are all liquids when the alkyl group is a straight-chained n-alkyl group of less than 18 carbon atoms. Di-n-octadecyldiphenylsilane, however, melts at 33-34°. A homolog of this compound, di-n-octadecyldi-p-tolylsilane, is also found to be a low-melting solid instead of a liquid. It seems, therefore, that the most favorable groups in the long-chained class for giving low-melting organosilicon compounds would be those which give alkyltriphenylsilanes whose melting points lie on the plateau mentioned previously, but which do not give solid R_4Si compounds. Then, the correlations point to the decyl- and dodecyl groups as being the most favorable ones.

Many compounds have been made by the author and others (see Tables 2-4) which have various combinations of long-chained n-alkyl groups with aryl groups. These will be discussed in some following sections.

Compounds containing aralkyl groups. Earlier in this Thesis (see

Table 17) attention was called to the fact that of the four isomeric C_7H_7 groups the benzyl one is the most promising for the purpose of introduction of low-melting points into tetraorganosilanes. From Table 1, it may be observed that three symmetrical tetraaralkylsilanes have been prepared and that the melting points of these decrease as the number of methylene groups increase. Thus, tetrabenzylsilane is the highest melting of these R_4Si compounds while tetrakis(γ-phenylpropyl)silane is the lowest melting one. However, the data in Tables 2, 3 and 4 show that for the three series of compounds, $R_3SiC_6H_5$, $R_2Si(C_6H_5)_2$ and $RSi(C_6H_5)_3$, another regular pattern is observed. In this pattern the melting point increases in the order R = γ-phenylpropyl < benzyl < β-phenylethyl. Thus, it would seem that the γ-phenylpropyl group is the most promising one for the lowering of melting points of tetraorganosilanes, then the benzyl group and lastly the β-phenylethyl group. The author has prepared several compounds containing both of the more promising groups, most of which have low-melting points.

Compounds containing halophenyl groups. Comparison of the m-fluoro- and the m- and p-chlorophenyl groups is possible since all compounds have been prepared in the series $(XC_6H_4)_xSi(C_6H_5)_{(4-x)}$ when the XC_6H_4 group is one of the three groups indicated and x is 1, 2, 3, or 4. All the compounds appear in Table 5. For each of the intergal values of x indicated, the m-fluorophenyl compound is the highest melting one. The m-chlorophenyl group gives the lowest melting compound for each value of x indicated except for the value of 2. For the case where x is 2, the m- and p-chlorophenyl compounds both have the same melting point;

for other values of x, the melting point of the para compound is intermediate to those of the two different meta compounds. The data would thus seem to indicate that the m-chlorophenyl group is preferable to either the p-chlorophenyl or the m-fluorophenyl as a device to give low-melting organosilicon compounds. Several organosilanes were prepared by the author and others (see Tables 2-4) which contained long-chained n-alkyl groups as well as the three different halophenyl groups. All these compounds were liquids except tris(m-fluorophenyl)-n-hexadecylsilane (m.p. 36-38°) and tris(m-fluorophenyl)-n-octadecylsilane (m.p. 38-39°).

Compounds containing phenoxyphenyl groups. Correlations of phenoxyphenyl groups must be limited to the o- and p-phenoxyphenyl groups since m-bromophenyl phenyl ether (needed to prepare m-phenoxyphenyllithium) was not available. In the $(C_6H_5OC_6H_4)_xSi(C_6H_5)_{(4-x)}$ series of compounds, all the o-phenoxyphenyl compounds have been made where x is 1, 2, 3 or 4, while all the p-phenoxyphenyl compounds were prepared except where x is 1. Apparently p-phenoxyphenyltriphenylsilane has not been prepared by anyone. As the data from Table 5 illustrate, the ortho isomer is the highest melting one in all three cases where both isomers are known. However, when x is 2, the difference in melting points is only two degrees.

Several compounds containing both phenoxyphenyl groups and long-chained n-alkyl groups were made by the author and others (see Tables 2-4); all of these compounds were found to be liquids and so no comparisons are possible as to the effect on melting point lowering.

Compounds containing tolyl groups. The melting point information in Table 17, page 112, shows that the m-tolyl group is the most favorable

one among the tolyl isomers as an aid to preparing low-melting organosilicon monomers. The author has therefore prepared a few compounds containing m-tolyl groups. n-Dodecyltri-m-tolylsilane (Table 4) was prepared and found to be a liquid which changes to a glass when cooled to -28°. The corresponding o- and p-tolyl compounds were not prepared, but comparison with n-dodecyltriphenylsilane, m.p. 67.5-68.0°, indicates a melting point lowering of ca. 80° with the addition of a methylene group in the m-position. Di-n-dodecyldi-m-tolylsilane was prepared and found to be a liquid which solidified to a glass upon cooling to -22°. No solid diaryldi-n-dodecylsilanes were available for comparison of the effect on melting point.

Compounds containing biphenylyl groups. Table 18, page 114, was presented in the Historical section. The data in the table illustrate the effect of the three isomeric biphenylyl groups on the melting points of tetraorganosilanes containing such groups. The data seem to indicate that the 3-biphenylyl group is the most promising one to be used in the preparation of low-melting organosilicon compounds.

During the present study, several 2-biphenylyl compounds were prepared, mainly for a study of steric hindrance as noted earlier. All the organosilicon compounds (including some not prepared by the author) which contained 2-, 3- or 4-biphenylyl groups in combination with long-chained n-alkyl groups were found to be liquids. These compounds are given in Tables 2, 3, and 4.

Compounds containing m-(trimethylsilyl)phenyl groups. Since m-tolyl

and m-biphenylyl groups cause melting point lowering in organosilicon monomers, it was reasoned by the author that the m-(trimethylsilyl)phenyl group should give compounds which melt lower than the corresponding compounds containing the p-(trimethylsilyl)phenyl group. Several compounds containing the latter group had been prepared by other workers; therefore, isomers of three of these compounds were prepared. n-Dodecyltris[m-(trimethylsilyl)phenyl] silane and phenyltris[m-(trimethylsilyl)phenyl]-silane were found to be liquid (the latter compound is very viscous at room temperature, however) while the corresponding p-isomers melt, respectively, at 68-75° and 189-191° (see Table 8). These data seem to confirm the author's view regarding the effect of the m-(trimethylsilyl)-phenyl group on the melting points of organosilicon compounds. However, it was found that tribenzyl[m-(trimethylsilyl)phenyl]silane melted at 68-70° while the corresponding p-compound[160] is a very viscous liquid at room temperature. The fact that the para compound is a liquid may be due to super-cooling.

Compounds containing biphenylene and (oxydiphenylene) groups. Since dissymmetrical groups appear to be favorable, in most cases, as devices to lower the melting points of tetraorganosilanes, the author felt that compounds such as those illustrated in Figures II and III would be valuable.

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[160]E. A. Zuech, private communication, Iowa State College (1957).

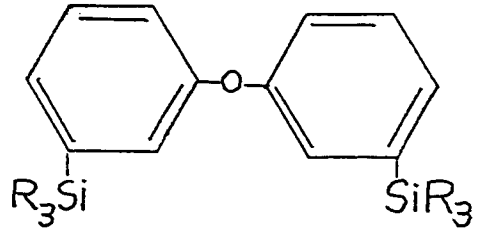

Figure II
An (oxydi-m-phenylene)bis[silane]

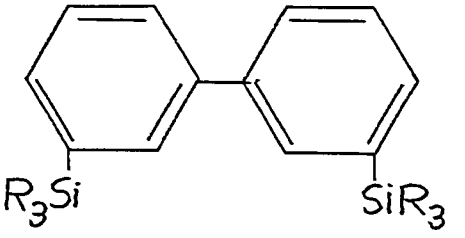

Figure III
A 3,3'-biphenylenebis[silane]

Compounds of the structure given in Figure II could not be prepared since bis(m-bromophenyl) ether was not available for the preparation of the required dilithium compound. However, some (oxydi-o-phenylene)- and (oxydi-p-phenylene)bis[silane] compounds, isomers of the structure given in Figure II, were made by the author. These compounds and one made by another worker are given in Table 8, Section E.

In Section C of Table 8 are listed several compounds having the structure of Figure III; in addition several compounds having structures isomeric to that of Figure III are given. The 3,3'-biphenylenebis[silane] compound (Figure III) were R is benzyl is interesting, since it melts twenty degrees lower than the 4,4'-isomer of this compound. A similar observation is found when the 3,3'-compound where R is methyl is compared to the corresponding 4,4'-isomer, i.e., the 3,3'-compound is a liquid while the 4,4'-isomer is a solid melting at 84°.

An interesting 4,4'-biphenylenebis[silane] compound is that formed from the reaction of chlorotri-n-hexadecylsilane with 3,3'-biphenylene-dilithium. The product, which gives a satisfactory silicon analysis and

a satisfactory molar refraction, distilled at 325-330° (0.05 mm.) which seems rather low for a compound having a molecular weight of 1561. An infrared spectrum of the product shows some disiloxane and a trace of an Si-H compound to be present and therefore indicates the product to be somewhat suspect. However, even though the product is somewhat impure, the fact that such a high molecular weight compound would distill at all is very encouraging from the standpoint of thermal stability.

Since compounds of the 3,3'-biphenylene type were found to be promising, it seemed probable that compounds of the type illustrated in Figure IV would also be of value, especially since a greater amount of dissymetry could be introduced into such a molecule.

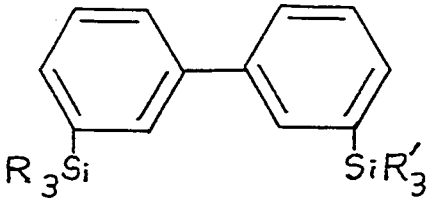

Figure IV
A 3-[3'(silyl)biphenylyl]silane

An intermediate compound, 3-(3'-bromobiphenylyl)tri-n-butylsilane, for the synthesis of these compounds was prepared. Difficulty was experienced, however, in attempts to convert the bromo compound to a lithium compound for further reaction. The author also prepared 3-(3'-bromobiphenylyl)trimethyl- and 3-(3'-bromobiphenyl)triphenylsilane as intermediates for the preparation of the compounds illustrated in Figure IV. Work on this phase was not completed, however. It is recommended that further study on these compounds be made.

Summary. It may be noted that two major methods of lowering the melting points of organosilicon compounds are available at present. The first of these is to introduce alkyl groups which are either long-chained n-alkyl groups (preferably n-decyl or n-dodecyl) or aralkyl groups (preferably γ-phenylpropyl, or benzyl). The second general method is to introduce dissymmetrical aryl groups (m-tolyl, m-biphenylyl, 3,3'-biphenylene, etc.) into organosilicon molecules.

Thermal screening relationships

The following discussion is devoted mainly to the effect of long-chained n-alkyl and aralkyl groups and to the effect of aryl groups on thermal stability.

Compounds containing long-chained n-alkyl groups. Among the symmetrical R_4Si compounds which contain only long-chained n-alkyl groups, the highest volatilization point (from Table 1) is found to be that of tetra-n-octadecylsilane which volatilizes at 464°. Most of the other compounds of this type volatilize in the range of 420-440°. A quick survey of all the compounds in Tables 1-4 which contain long-chained n-alkyl groups shows that the highest volatilization points of any of these compounds are those of di-n-octadecylbis(γ-phenylpropyl)silane and di-2-biphenylyldi-n-dodecylsilane. These volatilization points are, respectively, 470-480° and 475-480°. The volatilization of both compounds is accompanied by some signs of decomposition. If one compares volatilization points of the remaining compounds which have long-chained groups, it will be found that all of them lie between 400 and 470° with the exception of the one for dibenzyldi-n-octadecylsilane, which is given as 465-476° with no

apparent signs of decomposition.

Kinney[161] has given a formula, B.P. = 230.14 ^{3} B.P.N. - 543 (where B.P. is the boiling point and B.P.N. is the boiling point number), which is useful in calculating approximate values for the atmospheric boiling points of various compounds. In this formula, the boiling point number (B.P.N.) is the summation of a series of atomic or group boiling point numbers which are found empirically. Kinney, et al.[161] have given many of these atomic or group boiling point numbers for various atomic structures. More recently, Lewis and Newkirk[162] have published some values for silicon compounds and Spialter, et al.[129] have given some values for the 4-biphenylyl group in organosilicon compounds.

A tetraalkylsilane for which a Kinney boiling point calculation has been carried out is tetra-n-propylsilane. Lewis and Newkirk[162] calculated the group boiling point number for the propyl group in this molecule to be 7.85; they also calculated an atomic boiling point number of 4.20 for silicon in tetraorganosilanes. By using these values, and Kinney's values of 1.0 for the atomic boiling point number of hydrogen bonded to carbon and 0.8 for carbon bonded to carbon (in straight-chained molecules), the author calculated a B.P.N. of 158.8 for tetra-n-tetradecylsilane. Use of this value in the boiling point formula gives a boiling point of

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[161] C. R. Kinney, J. Am. Chem. Soc., 60, 3032 (1938); Ind. Eng. Chem., 32, 559 (1940); 33, 791 (1941); J. Org. Chem., 6, 220, 224 (1941); 7, 111 (1942).

[162] R. N. Lewis and A. E. Newkirk, J. Am. Chem. Soc., 69, 701 (1947).

ca. 700° for the compound. A similar calculation for tetra-n-octadecylsilane gives a B.P.N. value of 201.2 and a B.P. value of ca. 800°.

The approximate boiling points calculated for the long-chained R_4Si compounds may not be valid since a branching has occurred at the silicon atom and the molecule is therefore somewhat more symmetrical than a straight chain hydrocarbon. It was felt that, by using the values of Lewis and Newkirk[162] for the propyl group in tetra-n-propylsilane, correction for this symmetry factor might be partly effected. However, even if these calculated boiling points are in error by being as much as 100° too high, the boiling points of tetra-n-tetradecyl- and tetra-n-octadecylsilane would be, respectively, 600° and 700°.

It is noted that these calculated values are much higher than the observed volatilization points given in Table 1. It is the opinion of the author that the volatilization points of these compounds as well as all those of other compounds containing long-chained n-alkyl group are not true boiling points at all. Rather, they seem to be an observed decomposition point where the decomposition may be a thermal elimination reaction such as that depicted in Equation XVI.

$$RCH_2CH_2SiR_3 \longrightarrow RCH{=}CH_2 + R_3SiH \qquad \text{(XVI)}$$

In addition to the evidence already presented which indicates that the atmospheric boiling points of the compounds may actually be higher than the observed volatilization points, a second type of evidence may be found by converting the observed boiling points of these compounds at reduced pressure to the predicted ones at atmopheric pressure by use of a

"Pressure-Temperature Alignment Chart[163]." Using the boiling point of tetra-n-dodecylsilane reported in Table 1, such a calculation indicates the boiling point of this compound to be 490°, while that of tetra-n-hendecylsilane and that of tetra-n-tetradecylsilane are indicated, respectively, to be 530 and 510°. While these values are not as high as those predicted by the Kinney formula, they are significantly above the recorded volatilization points.

As evidence that Reaction XVI does indeed occur, the distillation of chlorotri-n-hexadecylsilane may be cited. When this compound was distilled under a reduced pressure which was such that a boiling temperature above 300° was needed for distillation, and then the product was redistilled, it was found that a large amount of an alpha-olefin (probably n-hexadecene-1) was obtained. Evidence in support of the identity of this product has been presented in Table 21, page 164. It also was observed that when the author distilled tri-n-decylsilane under a nitrogen atmosphere at slightly greater than atmospheric pressure, there were present in the infrared spectrum of the product bands indicative of the presence of an alpha-olefin. Distillations of several aryltri-n-hexadecylsilanes were found to yield products which had a band at 4.7 to 4.8 μ, thus indicating an Si-H compound was present in the mixture. The presence of such a band in the spectra seems to be evidence for the occurrence of Reaction XVI during the process of volatilization. It also is possible that the microbubbles observed during the volatilization process are the

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[163]Such a "Pressure-Temperature Alignment Chart" was distributed by the Matheson Company, Inc., East Rutherford, N. J., in 1950.

first indications of such a reaction. However, such microbubbles are noted in compounds which do not contain long-chained n-alkyl groups, and it is the author's opinion that they do not indicate decomposition.

In summary, it is felt by this worker that the upper limit of thermal stability of organosilicon compounds containing long-chained n-alkyl groups lies in the range of 400-480°. Since such groups are promising as functions with which to lower melting points, it is suggested that future work be restricted to those compounds containing only one group such as the decyl-, dodecyl- or perhaps octyl type since chains of this length seem most favorable as devices to lower melting points.

Compounds containing aralkyl groups. If one compares the volatilization points of tetrabenzyl-, tetrakis(β-phenylethyl)- and tetrakis-(γ-phenylpropyl)silane as given in Table 1, it is noted that the tetrabenzyl compound has the highest volatilization point. This value is about ten degrees higher than the values for the other compounds. Two grams of the tetrabenzylsilane was distilled (see Table 1) and the residue obtained was found to remelt at 110-118°. Recrystallization[8-I] of the product gave pure tetrabenzylsilane. Since tetrabenzylsilane has only one methylene group in each benzyl group, the compound could not undergo a decomposition such as that described in the previous section, while the compounds containing β-phenylethyl or γ-phenylpropyl groups might give such reactions. This fact might account for the slightly higher volatilization point of tetrabenzylsilane and also the value of the benzyl group in other compounds which will be described later. Comparison of the thermal screening values of benzyl-, β-phenylethyl- and

γ-phenylpropyltriphenylsilane given in Table 4 shows that they volatilize in the range of 428-442°. These may be true boiling points since one of the compounds was found to remelt within 3° of its original melting point after being heated at 428°.

In summary, it may be said that the benzyl groups appears to be very promising from both the melting-point lowering effect and from the standpoint of thermal stability. Of special interest are such compounds as 3,3'-biphenylenebis[tribenzylsilane] and (oxydi-p-phenylene)bis[tribenzylsilane]. For instance the biphenylene compound volatilizes at 520-530° and shows only slight signs of decomposition. The (oxydi-p-phenylene) compound (the most promising compound prepared during this study) volatilizes at 540-550° and shows only slight decomposition. This points to the fact that the benzyl group is very stable when compared to other alkyl groups; further compounds containing this group should be prepared.

Compounds containing aryl groups. The simplest way to compare the effect of the various aryl or substituted-aryl groups on thermal stability is to consult Table 5, Section A. This section list the symmetrical Ar_4Si compounds. Many of these compounds, unlike the tetraalkylsilanes have volatilization points well above 500°, although the upper limit seems to be about 570°. Table 22 is reproduced from an article by Spialter, et al. It shows the correlations between the observed boiling points and those calculated by the Kinney boiling point formula[161] for the 4-biphenylyl-substituted phenylsilanes, as well as that of tetraphenylsilane. The boiling point determinations of these workers were carried out in a special apparatus described by them; these are somewhat

Table 22. Boiling points of the 4-biphenylyl-substituted phenyl silanes

Compound	B.p., °C Found	Calcd.[161]
Tetraphenylsilane	430	428
4-Biphenylyltriphenylsilane	512	508
Di-4-biphenylyldiphenylsilane	570	573
Tri-4-biphenylylphenylsilane	580[a]	628
Tetra-4-biphenylylsilane	600 dec.[a]	678

[a]Significant decomposition occurred during the conditions of the boiling point determination.

more accurate than the thermal screening values reported in Tables 1-16. However, the data of Table 22 serve to point out that the volatilization points recorded in Table 5 for the tetraarylsilanes are probably true boiling points unless such volatilization points are extremely high (above 550°).

The aryl groups which seem most promising are the 3-biphenylyl, 2-naphthyl-, and o-phenoxyphenyl. These groups give Ar_4Si compounds volatilizing, respectively, at 570, 565-570, and 540°. Other promising groups are the p-phenoxyphenyl, p-chlorophenyl, and m-chlorophenyl groups. The groups having the higher molecular weights may be prefered in the preparation of organosilanes since they give correspondingly higher volatilization points.

Summary. From the standpoint of thermal stability, it would seem that the most promising groups to incorporate into organosilicon monomers are those chosen from the aryl, substituted-aryl and benzyl groups. Compounds which contain only one long-chained n-alkyl group may be favorable if a volatilization point lower than 480° is desired.

Suggestions for Further Research

The various correlations which have been made, suggest several future lines of research. Some of these have been mentioned previously, but are given again in the following list:

1. The most promising approach seems to be the preparation of compounds having the structure given in Figure IV, page 168. It is suggested that compounds where R is benzyl, and R' is phenyl, methyl, or n-butyl be prepared, for instance. A compound where R is benzyl and R' is m-tolyl also should prove interesting.

2. Since compounds containing alkyl groups seem to lose some of the desired thermal stability, it is suggested that compounds of the type ArAr'Ar''SiAr''' be prepared in an attempt to obtain low-melting compounds. One of these groups might be a benzyl group, although not an aryl group, since such groups show favorable thermal stability.

3. A supply of m-bromophenyl phenyl ether should be procured and compounds of the type $(m\text{-}C_6H_5OC_6H_4)_xSi(C_6H_5)_{(4-x)}$ be prepared where x is 1, 2, 3 or 4; this could then be compared with the corresponding o- and p- compounds. This study would involve a preliminary study of the halogen-

metal interconversion of the m-bromophenyl phenyl ether.

4. A supply of bis(m-bromophenyl) ether also should be procured and compounds of the type depicted in Figure II be prepared as well as compounds in which the two trialkyl- or triarylsilyl-groups are different. Again, preliminary halogen-metal interconversion studies would be involved.

5. A literature survey should be made of the reaction which occurs between organolithium compounds and R_3SiH compounds. Following such a survey, studies could be initiated on the effect of various alkyl and aryl groups on the rates of reaction between these compounds. Kinetic studies might be made by using acid hydrolysis and measuring the hydrogen liberated from any lithium hydride formed. It might be possible to use variously-substituted phenyllithium compounds and calculate a series of Hammett sigma and rho constants for the reaction.

6. Further studies should be made in a quantitative way to ascertain if organosilicon compounds containing long-chained n-alkyl groups do indeed undergo the thermal elimination reaction suggested as Reaction XVI. A typical experiment might be to heat tetra-n-dodecylsilane under a nitrogen atmosphere at a temperature near the recorded volatilization point for several hours. Samples might be removed intermittently and infrared spectra taken to observe whether any Si-H compound has been formed, or if any olefinic bands are present in the spectra. The mixture then could be distilled and any olefin or other products isolated and identified.

7. In connection with some recent studies not reported in this

Thesis, it has been observed that an apparent redistribution reaction occurs when diphenylsilane is heated in the presence of furan and chloroplatinic acid. The products of this reaction, in addition to starting materials, are phenylsilane, and triphenylsilane. It also is possible that some tetraphenylsilane may be formed although this has not been established. It is recommended that further studies on this reaction be carried to establish whether furan, chloroplatinic acid or heat is responsible for the rearrangement.

SUMMARY

A series of sixteen tables was compiled in which are listed the organosilicon compounds prepared in This Laboratory over the past several years. These tables were prepared in order that correlations between melting points, thermal stability and structural features could be made, and so that future workers in This Laboratory could apply these correlations to the synthesis of organosilicon monomers for possible use as thermally-stable, radiation-resistant lubricants or hydraulic fluids.

In connection with the tables, a complete bibliography of the publications from This Laboratory dealing with organosilicon compounds was prepared. This bibliography follows the tables.

A brief historical review was made of the recent literature on tetraorganosilanes having structural groups similar to those incorporated into the new compounds reported herein.

Several new organosilicon compounds were synthesized which incorporated long-chained n-alkyl groups, aralkyl groups, and various aryl groups. These were prepared in order to obtain low-melting organosilicon compounds of high molecular weight suitable to application of thermally stable lubricants and hydraulic fluids.

A study of the preparation of cyclohexyltriphenylsilane by several different methods was carried out. Some of these preparations were successful, others were not; possible reasons for the failures have been discussed.

A series of correlations about the effect of various groups on the melting point and the thermal stability of organosilanes was prepared.

Suggestions for future research based on the data gathered for and presented in this Thesis were made.

ACKNOWLEDGMENT

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